Review of the Canadian Chlor-Alkali Industry

Status of the Industry and Measures Taken for the Control of Water Pollution

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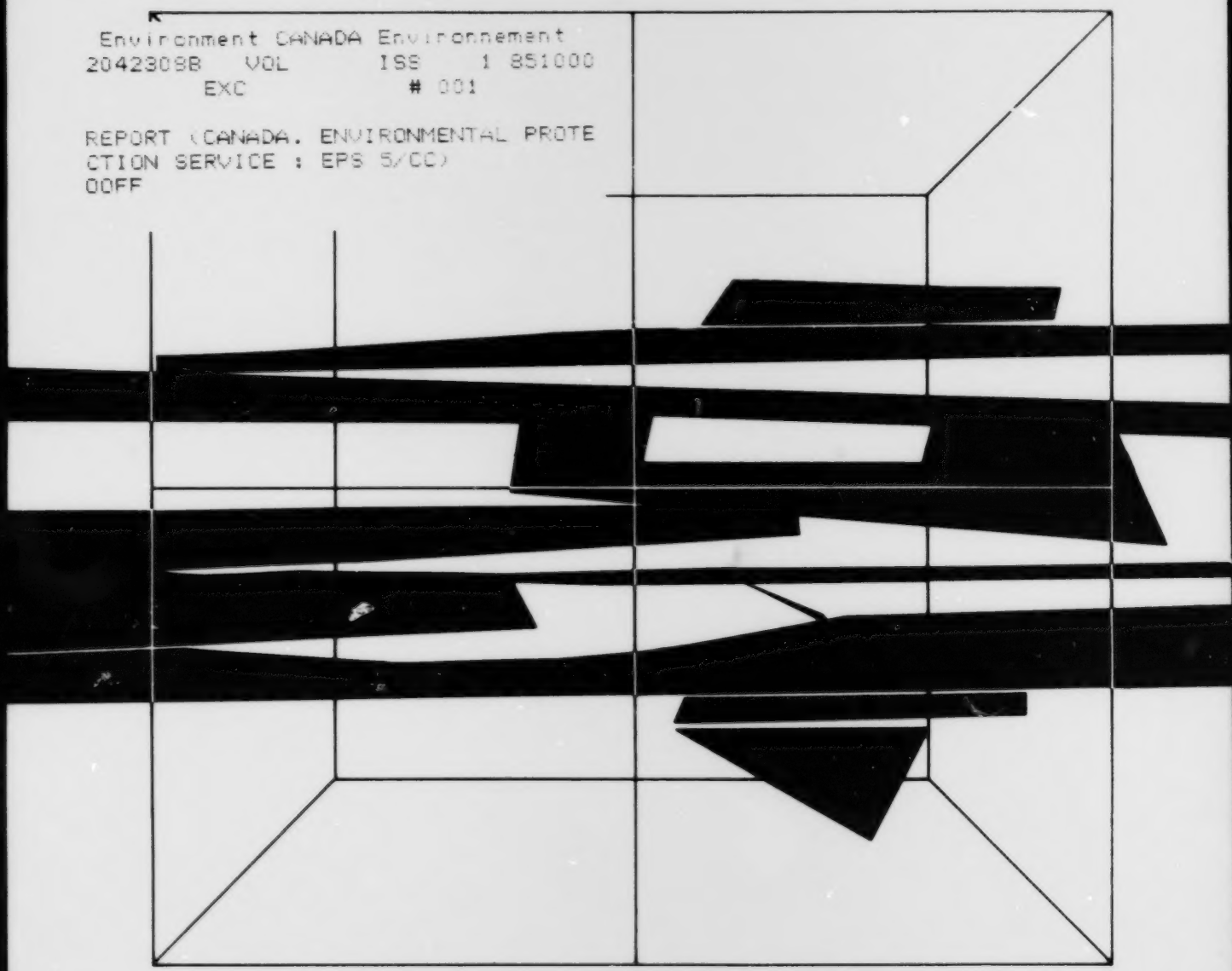

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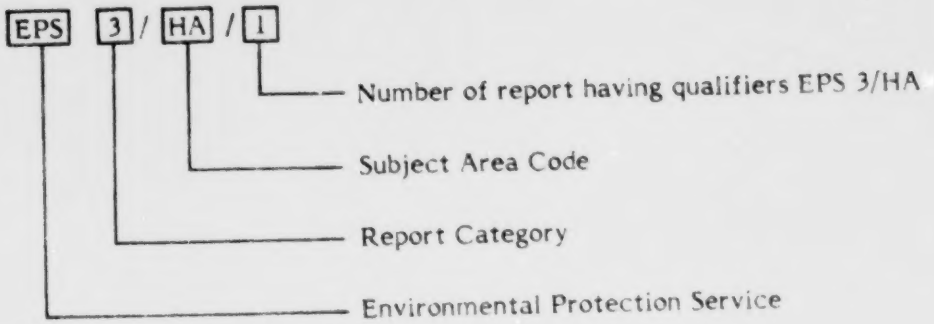

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REVIEW OF THE CANADIAN CHLOR-ALKALI INDUSTRY

Status of the Industry and Measures Taken for the Control of Water Pollution

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EPS 5/CC/1
October 1985

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ABSTRACT

This report reviews production processes, waste products produced, recycle and reuse of water, and other waste reduction practices, wastewater treatment practices, and concentrations and loadings of conventional and priority contaminants discharged into the final effluent from Canadian chlor-alkali plants. This information is based on surveys carried out during 1981-82 visits to chlor-alkali plants, company reports, and literature surveys.

The chlor-alkali industry and associated production technology has had a history of slow evolution; however, over the past ten years several significant changes have been implemented. Among the more important changes are:

the conversion from graphite electrodes to dimensionally stable anodes (DSA) at most, if not all, plants;

the development of treatment processes to eliminate nearly all mercury discharges in wastewater from mercury cell plants;

the conversion from mercury cells to the new ion-exchange membrane technology at two plants;

the elimination of all process wastewaters from one diaphragm-cell plant and the near elimination from two others; and

the marked reduction of process wastewaters from other diaphragm-cell and mercury-cell plants.

The process and treatment changes made at all chlor-alkali plants have significantly reduced conventional pollutant concentration in the wastewaters discharged, and virtually eliminated organic wastes produced in the chlorine purification process, where graphite anodes were used.

About 25 chlorinated organic contaminants were found, besides a number of metals. The metallic concentrations in the final effluent are too low to be treatable by conventional techniques. The organic pollutant concentrations are also low, ranging from trace levels to 260 micrograms per liter.

Biological testing of these straight effluents elicited no genotoxic activity. The effluent samples, after 250-fold concentration by extraction with methylene dichloride, were mutagenic to Salmonella, with the activity ranging from a two-to four-fold increase in mutant colony count. Two plant effluent extracts also exhibited chromosome-damaging activity and DNA repair inhibition. This should be no cause for concern; similar results have been found for finished drinking water supplies.

The report concludes that further regulatory initiatives by the federal government are not required at this time and recommends that this industry sector be looked at again in 5-7 years.

RÉSUMÉ

Le présent rapport est une étude des usines canadiennes de chlore, et plus particulièrement les points suivants ont fait l'objet d'une attention particulière: procédés industriels; production de résidus; recyclage et réutilisation de l'eau; autres techniques permettant de diminuer la quantité de résidus; méthodes de traitement des eaux usées; teneurs et charges en polluants classiques et prioritaires de l'effluent final par ces usines. L'information ainsi recueillie est fondée sur des observations effectuées lors de visites d'usines de chlore en 1981-1982, sur des rapports de compagnies et enfin sur la documentation existante.

L'industrie du chlore ainsi que les techniques de production utilisées ont connu une évolution relativement lente; mais, pendant les dix dernières années, plusieurs changements importants sont intervenus. Parmi les plus importants, on peut citer les suivants:

la conversion des anodes en graphite, en anodes à dimensions stables (ADS), dans la plupart sinon dans la totalité des usines;

la mise au point de procédés de traitement permettant d'éliminer presque tout le mercure déversé dans les eaux usées par les usines équipées de cellules à cathode de mercure;

le remplacement des cellules à mercure par de nouveaux dispositifs à membrane échangeuse d'ions dans deux usines;

l'élimination de toutes les eaux usées de procédé dans une usine équipée de cellules à diaphragme et l'élimination presque totale dans deux autres;

la baisse sensible de la quantité d'eaux usées de procédé, produites par d'autres usines équipées de cellules à diaphragme ou à mercure;

Les modifications apportées aux procédés et aux traitements dans toutes les usines de chlore ont permis d'abaisser sensiblement les teneurs en polluants classiques dans les eaux usées évacuées et, là où des anodes en graphite étaient utilisées, elle a permis d'éliminer presque complètement les résidus organiques produits lors de la purification du chlore.

N.D.T.: Dans le présent rapport, le vocable "usines de chlore" désigne les usines fabriquant du chlore et de la soude ou de la potasse.

On a décelé environ 25 contaminants organiques chlorés, plus un certain nombre de métaux. Les teneurs en métaux dans l'effluent final sont trop faibles pour être réduites par les techniques classiques. Les teneurs en polluants organiques sont elles aussi très faibles, allant de quelques traces à 260 microgrammes par litre.

Des essais biologiques avec les effluents bruts n'ont révélé aucune activité génotoxique. Des échantillons d'effluents, concentrés par extraction au dichlorure de méthylène, avaient des effets mutagènes sur *Salmonella*, l'activité pouvant doubler, voire quadrupler, si on considère le nombre de mutants par colonie. Les produits d'extraction d'effluents de deux usines ont également révélé des dommages aux chromosomes ainsi qu'une inhibition de la synthèse réparatrice de l'ADN.

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SUMMARY AND RECOMMENDATIONS

The chlor-alkali industry is a large and mature segment of the inorganic chemical industry. The production of caustic and chlorine is by the electrolysis of sodium or potassium chloride via three processes. In the two major processes the diaphragm cell and the mercury cell are used; the third, the ion-exchange membrane cell has been installed at three relatively small plants in Canada. Present Canadian caustic/chlorine production by the three processes are approximately 78 percent, 16.5 percent, and 5.5 percent, respectively.

All cells produce comparable grades of chlorine but different grades of caustic; e.g. the mercury cell produces a more concentrated caustic solution (50% NaOH) of higher purity than that obtained from the diaphragm cell (approx. 12.5% NaOH which must be evaporated to produce a 50 percent NaOH solution containing about 1 to 1.5% NaCl). The membrane cell, on the other hand, produces a very pure caustic at a concentration of 20 to 25 percent. This caustic can be concentrated to about 40 percent while passing through the heat recovery evaporator. An external heat source is required to concentrate the caustic from 40 to 50 percent.

The differences in cell design and associated unit processes results in differences in the quality and quantity of wastewaters generated; however, in-plant unit process changes, and wastewater recycle/reuse practices have significantly decreased the loadings of conventional and priority pollutants discharged from this industrial sector.

The main conventional pollutants discharged from chlor-alkali plants are acids or alkalines, suspended and dissolved solids, and residual chlorine. Steps taken by this industry to reduce these pollutants in wastewater discharges are summarized below:

Parameter	Steps Taken Toward Treatment	Results
pH	Acid and alkaline streams recycled/reused or neutralized	The pH of wastewater discharges normally within 6-9 range. Excursions between pH2-12 do occur.
Suspended Solids	Brine purification solids filtered or ponded. Solids sent to landfill, salt cavity, or ocean discharge.	S.S. concentration normally low, less than 25 mg/L.

Parameter	Steps Taken Toward Treatment	Results
	Cell renewal solids sent to authorized landfill site.	
Dissolved solids	Brine, acid and caustic leaks and spills collected and recycled.	Dissolved solids discharged average around 50 kg/kkg of chlorine produced. Some plants discharge higher values (230 kg/kkg).
Residual Chlorine	Tail gas scrubber effluent used, decomposed, and recycled or discharged. Chlorine containing wastewaters stripped, recycled, or reused.	Residual chlorine concentrations normally below 0.1 mg/L, but high excursions up to 100 mg/L do occur.

The main priority contaminants discharged from chlor-alkali plants are mercury (mercury-cell plants), asbestos (diaphragm-cell plants), priority metals, and chlorinated organics. Steps taken by the chlor-alkali industry to reduce these pollutants in wastewater discharges are summarized below:

Parameter	Steps Taken Toward Treatment	Results
Mercury	Mercury-contaminated waste waters recycled or sulphide-treated for Hg removal. Brine treatment solids high in mercury are retorted or leached for mercury recovery or buried in an authorized landfill site. Caustic filtered to remove Hg. Backwash recycled or treated. Hydrogen and vent gas condensates recycled or treated. All other Hg-contaminated wastewater treated for Hg removal.	Mercury discharges in final effluent from all plants very low. Average loading for the five plants is 0.51 gram per tonne of Cl_2 produce. Current requirement allows 2.5 grams of mercury per tonne of Cl_2 produced.
Asbestos	All diaphragm cell wash waters heavily laden with asbestos are kept separate and are either filtered and the solids, stored in drums and	Results from one plant indicate levels below one million fibers per liter. This concentration in industrial wastewater is not considered high as about 5 per-

Parameter	Steps Taken Toward Treatment	Results
	buried, or the slurry goes to a pond and the asbestos is sent to an authorized landfill site.	cent of the Canadian public receive water supplies with over 10 million fibers per liter.
Lead	Dimensionally stable anodes used at plants (with possible exception of three plants not disclosed). No lead used at any plants including the three unknown.	Lead levels in all plants low. Below levels for conventional treatment - 0.005 mg/L.
Other Metallics	Sulphide treatment to remove Hg from mercury cell waste waters probably removes other metallics.	Priority metallic concentrations low in all plants.
Chlorinated Organics	The small volume of chlorinated organic wastes associated with the use of graphite anodes was eliminated when DSA's were installed.	Some chlorinated organics like hexachlorobenzene should be eliminated and other chlorinated organic compound concentrations in discharged wastewaters substantially reduced.

Although mercury-cell plants have developed processes to enable them to comply with federal mercury liquid effluent regulations and to hold discharges to the atmosphere to reasonable levels, two-thirds of the mercury cell plants have either been closed down or been converted to the diaphragm and membrane processes in the past 12 years. Because of inherent problems with mercury pollution and because this process has no energy advantage over the newer types of diaphragm cells and membrane cells, the industry will probably limit its use to the five existing plants.

In the future, when the ion-exchange membrane cell will have been perfected to produce a strong caustic, a shift to this process is expected, because no mercury or asbestos is involved, and toxic contaminant (metals and chlorinated organics) concentrations in wastewaters should be as low or lower than in the other two processes. Also an evaporator purge is not needed, since the caustic is very pure, containing only insignificant amounts of sodium chloride and sodium sulphate.

Even though the volume of chlorinated organics has been significantly reduced with the conversion from graphite anodes to dimensionally stable anodes, the screening survey, which was undertaken at five plants for the identification and characterization of

priority pollutants in final effluents* from chlor-alkali plants, indicated that small amounts of priority chlorinated organics were still present in wastewaters discharged from this industry. Biological testing (Salmonella mutagenicity test) of straight effluents** found no mutagenic activity. However, final effluent samples, which were concentrated by extraction with methylene dichloride, demonstrated mutagenic activity (using Salmonella) in two sample extracts, chromosome-damaging activity in three effluent extracts, and DNA repair inhibition in two sample extracts.

Genotoxicity test data based on three effluent samples, however, are inadequate for the assessment of possible human health hazards and other environmental impact. Other factors which might have an influence on the environmental impact are:

i) the fate of the contaminants (bioaccumulation, biodegradation, volatilization, persistence, sorption, etc.)

ii) dilution of the effluent upon its entry into receiving waters,

iii) possibility of the effluent entering drinking water supplies or productive fishing waters, and

iv) fluctuation in the release of priority pollutants from industrial sources.

In summary, the industry, at the present time, does not cause severe water pollution problems. Liquid effluents containing non-toxic inorganic salts and precipitates are lagooned, and the supernatant water is recycled or reused in the plant system to a major extent. However, small amounts of asbestos fibers, mercury, residual chlorine, and priority organics in wastewater streams might be of environmental concern from a long-range viewpoint.

Since this industry has taken major steps to eliminate or reduce conventional and priority pollutants in its wastewaters and since final effluent samples concentrated 250 fold exhibit only low genotoxic activity it is recommended that no further action be taken at this time.

---

* Final effluent is defined as the total wastewater leaving the plant after final treatment, and may include once-through cooling water.

** Straight effluent is defined as the wastewater sample received by the biological laboratory; it has not been extracted using standard procedures. The straight effluent is normally a portion of the final effluent discharged from a plant.

This industrial sector should be looked at in 5 to 7 years. If future investigative work is required it is recommended that:

- individual streams be monitored for priority pollutants to determine whether any particular source can be identified, which could then be treated by more effective and economical means.
- that sample extracts for biological testing be fractionated in order to determine more easily the compounds causing the genotoxic activity.
- that efforts be directed to investigations of disposal areas for on-site brine solids, asbestos wastes, etc.

1 INTRODUCTION

1.1 Background

The Canadian chlor-alkali industry includes manufacturers not only of chlorine and caustic soda, but also of caustic potash. Caustic potash is not treated separately here, however, because of its low production volume. Also the environmental concerns about caustic potash production are similar to those of caustic soda production.

Chlorine and its co-product caustic soda are used in large quantities in the production of organic and inorganic chemicals, plastics, in the pulp and paper industry, in the aluminium industry, at water and wastewater treatment facilities, and in a number of other industries.

The production rate in Canada is about 1.4 million tonnes of chlorine per year. Of this amount, approximately 78 percent is produced by the diaphragm cell process, approximately 16.5 percent by the mercury cell process, and approximately 5.5 percent by the membrane cell process. The three processes differ in cell design and in the quantity and quality of wastewaters generated, thus they are addressed separately in the following sections.

1.2 Objectives of the Study

The objectives of this report are to review basic background information on

- the processes used in the chlor-alkali industry,
- in-plant control of wastewaters produced,
- the extent of toxic pollution discharges determined from the chemical analysis and flow measurements of representative process wastewater effluents, and
- the existing controls and treatment practices.

Prior to this study, most of the information available concerned conventional pollutant discharges from these plants. Any previous information on toxic pollutants was gathered from Environmental Protection Agency (EPA) studies indicating the presence of a few metallic and organic priority pollutants in effluents from this industrial sector.

This industry has a high water usage and even if low concentrations of the toxic substances are present, due to their persistence and the non-biodegradability of some of these pollutants, they have the potential to accumulate and have hazardous effects on fish and thus possibly on human health - on the environment generally.

1.3 General Approach and Methodology

In 1973 a questionnaire, drafted by the Environmental Protection Service (EPS) in cooperation with the Canadian Chemical Producers' Association, was sent to all chlor-alkali plants in Canada. The information received on wastewater flows, conventional pollutant concentrations, monitoring methods, and sludge disposal practices was compiled and used as a basis for the discussion on best practical control technology for this industrial sector.

In 1974 a task force was convened to provide a technical forum for consultation between the Canadian Chemical Producers' Association and the staff of environmental agencies from various provinces and the federal government.

Although many meetings were held, the task force was not able to reach a consensus on pH limits, limits for total suspended matter, and conditions for testing acute toxicity to fish. After the last meeting, in late 1978, all regulatory documents were updated to include all the issues discussed, but were never published as "Regulations".

Early in 1979, EPS proposed to undertake a screening study of industries for various toxic contaminants. The objective was to allow the Department to focus its resources on those industries and contaminants which give cause for concern. In 1980-81 a decision was taken to complete a review assessment of the chlor-alkali industry.

In-depth joint EPS - provincial screening surveys, with the full cooperation from the plant personnel - were implemented and carried out over a two-year period. Five plants, which should be representative of the diaphragm and mercury processes, were included in the surveys.

In general, 24-hour composite samples of the final effluent and intake water were collected over a three-day period. All conventional parameters were analyzed in the field or in EPS Regional laboratories, and the results compared to previous records. The toxic contaminants were analyzed at the EPS River Road laboratory in Ottawa. Biological testing for mutagenicity was carried out by the B.C. Cancer Research Centre in Vancouver, B.C. Details of these tests are presented in subsequent chapters.

2 MERCURY CELL PROCESS

2.1 Mercury Cell Process Description

The mercury cell, in general, consists of two sections: the electrolyzer and the decomposer or denuder. (Figure 1 is a schematic of the mercury cell.) The electrolyzer is usually a long, slightly sloped trough, either rubber-lined or made of bare steel, containing flowing brine for electrolysis. The cathode is a thin layer of metallic mercury completely covering and flowing down the bottom of the trough under the brine. The trough is covered, and projecting down through the cover are dimensionally stable anodes (DSA). Chlorine, produced at the anodes, leaves the cell through the chlorine headers to the drying and liquefaction system.

At the mercury cathode, the sodium ion is discharged to form a dilute sodium amalgam. This amalgam leaves the cell (Figures 1 and 2) and flows to the decomposer, a graphite-packed tower. Here, the amalgam comes is contact with demineralized water to form a 50-percent caustic soda solution plus mercury and hydrogen. The reaction can be represented by equation:

$$2\ Na{:}Hg + 2\ H_2O \rightarrow 2\ NaOH + H_2 + 2\ Hg$$

The sodium-free mercury is pumped back to the front end of the cell for reuse.

Chlorine gas from the cells is cooled to remove water and other impurities. The condensate is usually steam-stripped for chlorine recovery and returned to the brine circuit or discharged. The chlorine gas is then dried using concentrated sulphuric acid. The diluted acid is recovered and either used for pH control or sold. When chlorine gas is compressed and liquefied, there are always some non-condensible gases, known as tail gas, made up of an equilibrium mixture of chlorine and air. Tail gas is usually scrubbed with caustic or lime, generating a hypochlorite solution, which is decomposed, used on-site, sold, or discharged with or without treatment.

The sodium hydroxide formed at the denuder has a concentration of about 50 percent NaOH. Because the caustic is formed outside the cell, it is salt-free and can be kept iron-free, since it normally does not have to be pumped through an evaporator system unless 76 percent caustic or caustic flake is required. Some impurities, such as mercury, are removed or reduced by filtration supplemented by filtering aids and, in some cases, activated carbon.

Hydrogen gas is refrigerated to remove water vapour and mercury. At some plants it is further treated with sulphur-treated, activated carbon, scrubbed using

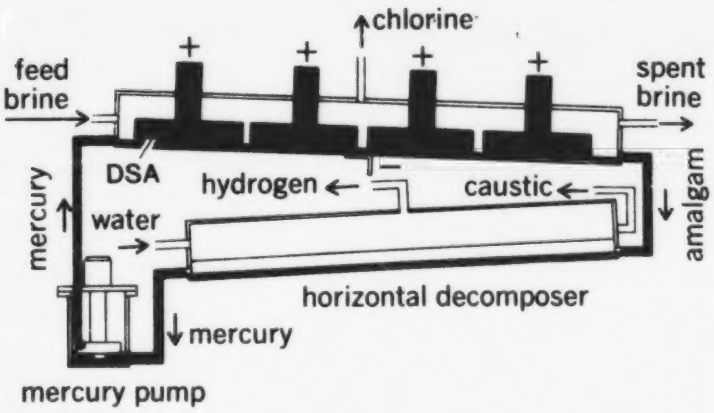

FIGURE 1 SCHEMATIC DIAGRAM OF MERCURY CELL

chlorinated brine or passed through molecular sieves. Condensate from hydrogen cooling is then discharged, after mercury recovery, or recycled to the denuder.

2.2 Water Use and Wastewater Sources

2.2.1 Water Use. Water is used at mercury cell plants for non-contact cooling, tail gas scrubbing, cell washing, floor washing, equipment maintenance, and sodium hydroxide production. A minimal amount of makeup water is required in the brine circuit and other areas of the plant. These requirements, however, are normally met by recirculation or reuse of water; e.g., the inlet and outlet endboxes of the cells are sealed by flooding with cooled, recirculated water. Water condensed in the hydrogen cooler and cell ventilation cooler is reused for inlet endbox cooling, and the chlorine cooler condensate may be reused as makeup water in the brine circuit.

The total water usage at plants was found to range from 6.6 to 210 cubic meters per tonne of chlorine produced, with non-contact cooling water comprising approximately 0 to 98 percent of the total. The EPA figures for comparable plants range from 7.6 to 204 cubic meters per tonne with approximately 70 percent of the total being cooling water.

2.2.2 Wastewater Sources

Dissolver Slurry

The major raw material for the chlor-alkali process is a nearly saturated solution of sodium chloride made from dissolving either rock salt or solar-evaporated salt in the depleted brine recycled from the cell. If rock salt is used, only about 94 to 98

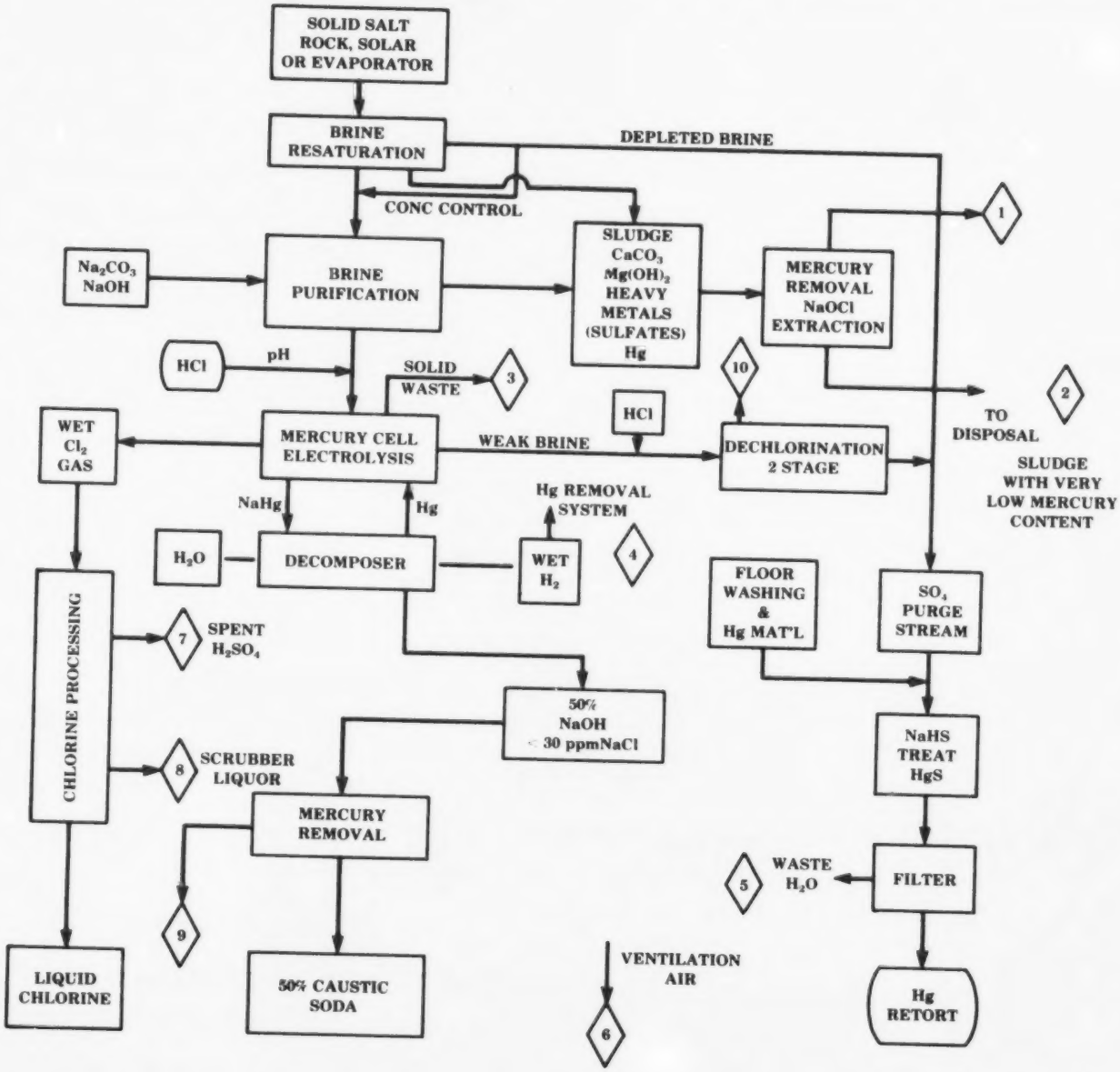

FIGURE 2 MERCURY CELL PROCESS SHOWING LOCATION OF POSSIBLE MERCURY LOSSES

percent of the rock salt is dissolved (the rest is anhydrite and gangue), resulting in about 30 to 100 kg of waste solids per tonne of chlorine produced. If the solids are filtered, they still contain some mercury, since the recycled brine containing soluble mercury is not entirely removed in the filter wash cycle. If brine sludge ponds are used, the brine is recycled; however, any seepages contain some brine, which contains mercury in low concentrations.

Brine Mud

The crude brine from the saturator must be purified further before it is suitable for use as a feed to the cells. This is carried out by adding barium chloride, sodium hydroxide, and sodium carbonate to raise the pH to a range between 10 and 11. The impurities most commonly removed during purification are calcium, magnesium, sulphate, iron, and such trace metals as chromium, titanium, molybdenum, vanadium, and tungsten. Heavy metals and magnesium are precipitated as hydroxides, and calcium as a carbonate or sulphate. A flocculating and settling aid is usually added to enhance the settling of the precipitates. The waste sludge is normally filtered and then sent to landfill sites or sluiced to a pond. The amount of solids produced in the brine purification step depends upon the salt purity, but averages about 15.6 kg per tonne of chlorine produced. In addition, the solids occlude about 3 kg of NaCl per tonne of chlorine produced.

In the mercury cell process, only about 16 percent of the NaCl solution is decomposed in the cell, thus the brine, which is recycled, will be contaminated with mercury, hence the brine mud also contains small amounts of mercury.

Cell Room Wastes

The major components of cell room wastes includes leaks, spills, brine header blowdown, bleed from the endbox cooling stream, general housekeeping, and cell wash waters. The amount varies from plant to plant and depends on operating practices. Cell room wastewaters constitute the major stream requiring treatment for removal of mercury.

In the past, graphite anodes were used in the cells, thus the wastes contained lead and chlorinated organics such as hexachlorobenzene. All of the mercury-cell plants in Canada, however, are now using dimensionally stable anodes.

Chlorine Condensate

Condensate from the chlorine gas cooling system is normally saturated with chlorine. This stream is stripped to remove the chlorine and subsequently recycled to the

process or directed to the plant effluent stream. For this reason the amount and type of wastewater varies, but normally is around 50 to 100 litres per tonne of chlorine produced.

Spent Sulphuric Acid

Concentrated sulphuric acid is used in the drying tower to remove residual water from the chlorine gas after the first stage of cooling.

The spent sulphuric acid, at a strength of 50 to 70 percent at a flow of around 7 to 10 litres per tonne of chlorine produced, is constantly bled from the drying towers. This acid is normally passed through a steam-stripping operation for chlorine removal. The spent acid can be regenerated, used for pH control or sold for other uses; e.g., fertilizer production.

Tail Gas-Scrubber Liquid

Intermittent chlorine vent gas, such as uncondensed chlorine gas from the liquefaction stage, residuals in tank cars, purged equipment, etc., is scrubbed with sodium hydroxide or calcium hydroxide to form either a sodium or a calcium hypochlorite solution.

The hypochlorite can be used on-site, sold, discharged to treatment systems, or decomposed before discharge. The amount of tail gas scrubber water varies from plant to plant but normally varies from 0.15 to 0.5 cubic meter per tonne of chlorine produced. At most of the plants some of the weak chlorine gas is used in the manufacture of hydrochloric acid.

Caustic Filter Washdown

The 50-percent caustic is filtered to remove mercury and other impurities. The filters are periodically backwashed, and this low water flow is sent to a holding tank. The solids, which settle out, are normally retorted for mercury recovery. The supernatant is sent to the brine treatment system, recycled to the caustic circuit, or sent to the mercury sulphide treatment system.

Hydrogen and Vent Gas Condensates

Hydrogen produced at the denuder and vent gases evacuated from the endbox are normally cooled in two or three stages to remove mercury and water carried over by the gas. The gas is initially cooled by indirect cooling in primary water-cooled heat exchangers. The condensate is returned to the process, or if the need arises, the condensate goes to the sulphide treatment system.

Boiler Blowdown

The boiler blowdown contributes about 10 to 15 litres of wastewater per tonne of chlorine produced. This stream usually contains sulphates, sulphites, phosphates, silica, carbonates, suspended solids, and some metallics.

Cooling Tower Blowdown

Relatively large quantities of cooling water are required in the chlor-alkali manufacturing process. This water, which can be drawn from the sea or from fresh-water sources, does not normally come in contact with any process chemicals.

This cooling water can either be a once-through flow or be recycled through a cooling tower. If cooling towers are used, a blowdown is required to control the concentration of those impurities and contaminants that could be scale-forming. The usual contaminants found in this stream are sodium, calcium, magnesium, chloride, sulphate, nitrate, and some corrosion inhibitors such as chromates, zinc, phosphates and silicates as well as a biocide such as chlorine.

Sanitary Effluent and Laboratory Drains

Sanitary effluent, including clothes-laundering effluent, is directed to municipal sanitary systems or to septic tanks. Overflow from septic tanks and laboratory drains is normally discharged without treatment along with the treated wastewater from the plant. The flow from the five plants in Canada ranges from 100 to 500 litres per tonne of chlorine produced. This effluent contains some mercury, which is normally included in the figure of total plant discharge.

Storm Runoff

Storm runoff from the processing areas (including roof drains) and the storage of raw materials, finished products, and waste materials can vary in degrees of contamination depending on yard-keeping practices, and volume and frequency of rainfall.

At most plants, some of the storm water is treated for mercury removal. Mercury present in untreated storm water is normally included in the daily monitoring required of each plant.

Summary of Wastewater Flows

Flow rates of process wastewater from mercury cell chlor-alkali plants average around 3 m^3/kkg of chlorine produced (Table 1).

TABLE 1 SUMMARY OF WASTEWATER FLOW DATA FOR CHLORINE MERCURY CELLS PLANTS

Plant Number	Wastewater Flows (m^3/tonne Cl_2)		
	From NaOH, Cl_2	From HCl	Total
1	0.73	3.0	3.73
2	4.5	4.4	8.9
3	5.62	-	5.62
4	1.69	-	1.69
5	2.32	3.3	5.62

Thirteen mercury-cell plants in the USA average rates of wastewater flows at 2.1 m^3/kkg, although flows as high as 6.3 m^3/kkg do exist.

The values at Canadian plants are higher than those at USA plants, because boiler and cooling tower blowdown have been included.

2.3 Conventional Pollutant Concentrations - Analytical Data

2.3.1 Methodology. The collection of detailed analytical data on conventional pollutant concentrations in process wastewater streams was completed in a three-way data-gathering system. In 1973 a questionnaire was distributed to all mercury cell chlor-alkali plants requesting detailed information on flows and pollutant concentrations present in process and cooling waters.

Over the past eight years, a number of surveys by EPS Regional personnel and by their Provincial counterparts have been carried out. All plants are required through regulation to submit, on a monthly basis, total flow and mercury losses to liquid effluents. In addition, some of the plants are required to submit monthly monitoring data (i.e. pH, residual chlorine, suspended solids, etc.) to their Provincial Ministry for the Environment.

2.3.2 Description of Specific Plants. The following discussion primarily covers plant practices in water pollution control and treatment of wastewaters from mercury cell chlor-alkali plants still operating in Canada.

Plant No. 1

Plant No. 1 was modernized and expanded in 1970, at which time the old mercury cells and cell buildings were demolished and replaced with modern mercury cells

in a new building. The drainage system from the old chlorine plant was no longer required and therefore blocked off. Later it was found that infiltration into the old sewer pipes was contributing to mercury losses; so these sewer lines were blocked off at both ends.

At this plant depleted brine from the cells is sent to two saturators, where rock salt is added to increase the salt concentration to around 310 g/L. The build-up of solids (mainly anhydrite) in the bottom of the saturators is periodically flushed in to a sludge tank. This sludge is pumped to a vacuum filter for dewatering and then carted off for disposal.

The saturated brine overflows the saturator into three reaction tanks in series, where soda ash, caustic soda, barium carbonate, and lime are added to precipitate calcium, magnesium, sulphate, iron, and other minor impurities. The brine is then filtered to remove the solid impurities. The filtered brine goes to a storage tank for pure brine, where HCl is added, then through a brine cooler before entering the head tank from where the brine flows by gravity to each cell.

The lean brine leaving the cells goes to a surge tank and then to anolyte tanks, where some chlorine gas is collected and added to the main chlorine stream. The brine then passes through a vacuum degasification tank, where most of the remaining chlorine gas is stripped from the brine solution. Part of the brine stream is recycled to the circuit of pure saturated brine. Caustic soda is added to the rest of the lean brine, before being recycled to the saturators.

Solids from the brine filter backwash go to a sludge tank from where they are pumped to the vacuum filter (the same filter used for the saturator sludge). These combined solids, which contain 95 to 150 mg mercury per kilogram of sludge, are leached with sodium hypochlorite for mercury removal and recovery, before being buried in an approved landfill site. The filtrate from the vacuum filter goes back to the third brine reaction tank.

Any brine leaks, flush water used on the brine filter bearings, the seal water from the filter vacuum pump, anolyte seal-pot wastewater, chlorine water, disposal seal wastewater, and any cleanup wash waters from this area are collected and sent to the treatment system.

A standby tank collects brine in the event of a major process upset. If the larger brine tanks cannot hold all the brine, the excess automatically drains into this tank. Other small flows can also be diverted to this standby tank.

The hot, wet chlorine gas from the cells is initially cooled in two indirect coolers in series. The first cooler uses cooling water that is then recycled to the cooling

towers. The second cooler uses well water that is discharged into the sewer. The gas then passes through a demister, four sulphuric acid-drying towers in series, a dry chlorine demister, a compressor and a first-stage Freon liquefaction unit. Liquefied chlorine is sent to storage, while the remaining gaseous portion passes to a second-stage liquefaction unit. Any residual chlorine gas is scrubbed in a caustic soda absorption tower. The weak sulphuric acid is bled into the sewer.

Waste chlorine gas from the cell's dirt-box ventilation, and waste sulphuric acid receivers, as well as venting from air-padded vessels and tank car are sent to the caustic soda absorbers. The sodium hypochlorite solution is sold.

In the denuder, sodium-mercury amalgam, in contact with deionized water, is broken down to form caustic, hydrogen, and mercury. The mercury is pumped back to the head of the cell. The addition of deionized water is controlled, so that a 50-percent caustic solution is formed. The water also acts as a seal on the inlet to the denuder. The caustic formed in the denuder flows to a separator followed by two receiving tanks. From here the caustic is pumped to a cooler and then to a filter to remove impurities. The caustic, now containing less than 1 ppm of mercury, is sent to storage.

Occasionally the caustic filter is backwashed into a storage tank. After settling, the supernatant caustic solution is recycled to the brine treatment system. The mercury solids are stored for a period and then sent to a landifll site. All effluents are either recycled or sent to the mercury treatment system. These effluents may issue from floor drains in the caustic receiving and storage areas and in the caustic loading area, from pump leaks, seal water, etc.

Twenty-percent caustic, which is required in the operation of the plant, is made by diluting 50-percent caustic soda with filtered river water.

The hot hydrogen gas coming off each denuder passes through individual water-cooled primary coolers (to about 24°C) and then is combined to pass through a water-cooled secondary cooler (to 18°C). The cooled gas is then passed through a bed of activated carbon, impregnated with sulphur, and then compressed. This hydrogen gas is mainly used for fuel in the boiler house.

All the condensate from the primary coolers flows back to the denuders. The condensate from the hydrogen headers and secondary cooler is either recycled to the brine circuit or sent to the mercury treatment system.

A ventilation system on the cell inlet endboxes prevents the escape of gaseous mercury to the cell room. The gas being treated is cooled in a water-cooled, indirect

cooler and then passed through a bed of activated carbon impregnated with sulphur. The condensate collected from this system goes to the deionized water feed tank.

Water used for cooling/sealing mercury at the cell endboxes is sent to a recirculation tank. Water from this tank is cooled and recycled to the system. A purge stream is bled to the cell flush water to prevent a buildup of impurities (water is used to flush and cool cells taken out of service). This cleaning water, which contains mercury and brine, is collected and reused or recycled to the brine circuit.

Mercury-contaminated streams which are not reused or recycled (e.g. floor wash waters, some condensates, etc.) are collected and treated. The treatment system comprises:

- surge tanks,
- treatment tanks where the pH is adjusted, chlorine destroyed, and sodium hydrosulphide added to precipitate HgS,
- a filter, and
- an activated-carbon polishing absorber.

The mercury sulphide solids are mixed with the brine treatment solids prior to the sodium hypochlorite leaching step. As already indicated, these treated solids are buried in an approved landfill site.

Wastewaters low in mercury are discharged without treatment. Examples of such wastewaters are:

- waste sulphuric acid,
- miscellaneous chlorine condensates,
- boiler and demineralized water treatment effluents,
- some indirect cooling waters and cooling tower blowdown,
- wastewaters from the chlorine liquefaction and storage areas, maintenance areas, caustic loading area,
- some storm runoff, and
- sanitary effluent

These wastewaters, however, as well as the mercury-treated effluents are monitored 24 hours. Data available on discharges of conventional pollutants from this plant are shown in Table 2.

TABLE 2 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 1, CHLOR-ALKALI-MERCURY CELL

Parameter	PROCESS EFFLUENT				SANITARY EFFLUENT				STORM RUNOFF			
	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/1dkg)	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/1dkg)	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/1dkg)
Flow (m^3/d)**		25000				100*				23*		
pH**	19	10.2	1.5-12		20	11.3	9.2-11.9		25	9.5	7.9-11.5	
Total Solids	2	760	660-860	122.6	1	7400		4.8		820		0.12
Susp. Solids	6	143	13-310	23	1	3000		1.9	1	10		0.001
Dis. Solids	3	650	600-770	104.8	1	4400		2.8	1	810		0.12
TKN	6	2.2	0-11.2	0.35								
Total P	3	0.03		0.005								
Sulphate	2	160		25.8	1	490		0.3	1	101		0.015
Chloride	3	195	88-248	31.5	1	3700		2.4	1	300		0.04
Sodium (Na)	3	365	205-480	58.9	1	2380		1.5	1	185		0.03
Calcium (Ca)	3	33	30-36	5.3	1	40		0.03	1	73		0.01
Iron (Fe)	3	0.43	0.3-0.6	0.07	1	0.40		0.0003	1	0.04		0.000006
Mg	3	14.5	12-16	2.34	1	21		0.013	1	20		0.003
K	3	2.5		0.40	1	7		0.005	1	3.6		0.0005
Al	3	< 1			1	0.8		0.0005	1	< 0.25		
R Cl_2	23	30	0-2000	4.8	320	0	0		320	0		
Conductivity, umho/cm												
Hg	730	0.005	0.001-0.082	0.0008	14	5500	1700-8000		8	12000	1800-70000	
Cr	3	< 05			39	0.39	0.03-1.05	0.0003	39	0.02	0.001-0.325	0.000003
Cu	3	0.06	0.02-0.13	0.010	1	0.02		0.00001	1	< 01		
Ni	3	0.01		0.002	1	0.05		0.00003	1	< 01		
Pb	3	< 02			1	0.13		0.00008	1	0.02		0.00003
Cd	3	< 01			1	< 01			1	< 01		
Zn	3	3	0.03-9	0.48	1	0.02		0.00001	1	< 01		
Mn					1	0.10		0.00006	1	0.02		0.00003
					1	0.25		0.0002	1	0.10		0.00001

* For time period sampled.
** Units given in the column heading do not apply here.

Plant No. 2

At Plant No. 2 both sodium and potassium brines are used to manufacture sodium hydroxide and potassium hydroxide. With few exceptions the two processes are identical. Besides chlorine and both forms of caustic, the plant also produces hydrochloric acid, hydrogen, and sodium hypochlorite.

Depleted brine from the cells is sent to the saturator, where rock salt is added to increase the salt concentration to 25 percent. The build-up of solids (mainly anhydrite) in the saturator is removed once per shift to an inclined pit. The brine decanted from the pit is returned to the brine circuit. The solids are later removed to a disposal site on the plant property. The saturated brine is sent via a pump tank to a dechlorinator, then on to a reaction tank, where caustic and soda ash are added to precipitate calcium, magnesium, sulphate, iron, and other minor impurities in two clarifiers. The underflow from the clarifier is normally filtered. The filtrate is recycled to the brine circuit, and the solids are sent to an on-site sludge disposal area. When the filter is not operating, the brine treatment solids are sent to a sludge pond. Sludge from the pond is removed to an on-site disposal area every two years. Brine leaving the clarifier flows to a direct-air cooler, than to the brine holding tanks, before entering the cells. Any leaks from the brine pumps, tank overflow, equipment-cleaning, and brine purges in the cell room are directed to the mercury treatment tank.

The KCl brine circuit is slightly different, although based on the same principles. Depleted brine, after being dechlorinated and neutralized, is sent to a dissolver where solid evaporated KCl salt is added. Caustic potash and a carbonate brine are added to precipitate any impurities present in the saturated KCl brine, which then flows to a clarifier. The overflow from the clarifier is pumped to a head tank from where the brine flows by gravity to the cells. Clarifier sludges are pumped to the on-site sludge lagoon. Any brine leaks or spills are directed to the mercury treatment system.

Hot, wet chlorine gas from the cells and brine receiver tank are initially cooled in an indirect water-cooled heat exchanger. The chlorine condensate is returned to the saturator, and the cooling water is recycled to the cooling tower. The chlorine passes through a demister and then through a 2-by-3 array of H_2SO_4 drying towers, followed by a compressor, York demister and Freon chiller. Liquid chlorine is sent to storage, while the remaining gaseous portion passes through a mist eliminator and then goes to the HCl plant. The weak sulphuric acid bled from the first drying tower is sent to another plant for reuse.

Hydrochloric acid is produced by burning the residual chlorine gas in a slight excess of hydrogen. The gaseous hydrochloric acid generated in the burner is passed through a spray tower where it is absorbed in water. The HCl leaks are treated in a limestone tower before being discharged into the sewer.

In the denuder, sodium mercury amalgam, in contact with soft water, is broken down to form caustic, hydrogen, and mercury. The mercury is pumped back to the head of the cell. The soft-water addition is controlled, so that a 50-percent caustic solution is formed. The soft water also acts as a seal on the inlet to the denuder. The caustic formed in the denuder flows into a receiving tank. From here the caustic is pumped to a filter to remove impurities. Typical mercury concentrations of unfiltered caustic are 2 to 10 mg/L and of filtered caustic 0.2 to 0.5 mg/L. The filtered caustic is sent to storage tanks. The filter sludge is sent to a recovery tank, where the supernatant is returned to the caustic receiving tank. The recovered solids are retorted to recover mercury. All effluents from floor drains in the caustic receiver and storage tank areas, caustic loading area, pump leaks, etc. are either recycled or sent to the mercury treatment tank.

The hot hydrogen gas leaving the denuder is initially cooled in individual indirect water-cooled coolers. The condensed mercury and condensate flows back to the denuders. The cooling water is recycled to the cooling tower. The hydrogen is further cooled in a direct-contact spray cooler using soft water. The cooling water is recycled to the soft-water head tank used to supply the denuders. A tertiary indirect Freon heat-exchanger further reduces the hydrogen temperature to around 5°C before it passes through a mist eliminator. Some of the hydrogen gas is used to produce HCl, some is used in an adjoining carbon bisulphide plant incinerator, some in the mercury retort, and the rest is vented to the atmosphere.

A ventilation system is also used on the cell endboxes and denuders to prevent releases of contaminated, gaseous mercury to the cell room. These gases are treated in an indirect Freon cooler and mist eliminator. The condensate from this system goes to the soft-water denuder feed tank.

Sludges rich in mercury are retorted for mercury recovery. The mercury-laden vapours are condensed and the mercury is trapped in water pots. The water vapour condensed in the system is sent to the mercury treatment system. The cooling water from the condenser is sent to the sewer. The retorted solids, which contain about 10 ppm mercury, are sent to a landfill site.

All liquid wastes contaminated with mercury, including effluent from the sludge pond, are directed to a treatment system. The contaminated liquid wastes

requiring treatment, between 13.6 and 31.8 m^3/d, are pumped to a 80-m^3 hold-up tank. This tank is drained at a rate of 90 Lpm into a 1.4-m^3 reactor tank. The pH of the wastewater in the reactor tank is adjusted to between 6 and 8, and then sodium hydrosulphide and ferrous sulphate are added. The treated water is pumped to a 15-m^3 settler from which it overflows to a sand filter followed by an activated-carbon filter before being discharged into the plant sewer.

Solids removed from the settler are stored in a sludge holding tank. The sludge is later filtered and the liquid fraction is recycled to the hold-up tank, while the solids are transferred to the retort tank for mercury recovery. Backwash from the sand filter and the activated carbon filter are directed to the sludge holding tank. The carbon in the activated-carbon filter is periodically replaced, and the mercury recovered.

Wastewaters low in mercury, including cooling-tower blowdown, some indirect cooling water such as that used on the retort, water softener backwash, laboratory effluents, roof drainage, some seal water, any brine from the destruction of hypochlorite and wastewaters from the chlorine and hypochlorite plant, are discharged without treatment. As mentioned before, waste waters from the HCl area pass through a limestone tower.

The combined wastewaters from the plant pass through a flow-measuring device and automatic sampler.

Sanitary effluents go to the municipal sanitary sewer.

Table 3 presents conventional pollutant concentrations and loads for the sampled streams from this plant.

Plant No. 3

At Plant No. 3, solar evaporated salt is dissolved in depleted, recycled brine. The saturated brine, which now contains impurities such as calcium, magnesium sulphate, and other minor impurities is purified by adding sodium carbonate, caustic soda, and a flocculating agent. The precipitated material is drained from the clarifier to a sludge treatment tank. The brine solution, from the clarifier overflow, is heated and sent to the mercury cells.

Water used for cooling and sealing mercury at the cell inlet endbox and mercury pump tank is sent to a recirculation tank. Water from this tank is cooled and recycled to the inlet endbox. A purge stream is continuously bled to the decomposer. Cooling water from the outlet endboxes is cooled and recycled. Because of a buildup of NaCl, a purge is sent to the mercury treatment system. In addition,

TABLE 3 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 2 CHLOR-ALKALI-MERCURY CELL

Parameter	Intake Water (mg/L)	FINAL EFFLUENT No. of Values	Ave. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow (m^3/d)*			1715		
pH*	6.0	11	7.0	5.0-8.5	
Total Solids	180	11	1810	1100-3480	25
Suspended Solids	< 1	11	21	5-47	0.28
Alkalinity ($CaCO_3$)	70	3	60	51-65	
NH_3/N	0.1	3	0.2		0.003
TKN	0.4	3	0.9	0.2-2.1	0.012
Total P	0.1	3	< 0.1		
Sulphate (SO_4)	27	5	115	100-140	1.6
Sulphide (S)	0.1	3	< 0.1		
Chloride	28	11	720	400-1550	7.1
Sodium (Na)	64	5	500	250-880	6.9
Calcium (Ca)	36	5	55	47-60	0.7
Iron (Fe)	0.1	3	1.2	0.6-2.3	0.016
Fluoride	0.5	3	0.52	0.48-0.55	0.007
Magnesium	7.8	3	7.6	6.6-9.4	0.10
Potassium	3.4	3	106	94-112	1.45
Barium	0.023	3	0.04	0.02-0.05	0.0005
Aluminum	0.06	3	0.07	0.07-0.08	0.0010
Tin	0.026	3	0.023		0.0003
Chromium	< 0.01	3	< 0.01		
Manganese	0.01	3	0.04		0.0005
Lead	< 0.01	3	< 0.01		
Zinc	0.27	3	0.15		0.002
Thallium	0.01	3	0.03		0.0004
Cobalt	0.01	3	0.02		0.0003
Molybdenum	0.009	3	0.028		0.0004
Mercury		360	0.034	0.009-0.279	0.0004
Cadmium		1	< 0.05		
Copper		1	< 0.10		
Nickel		1	< 0.20		

* Units in the column headings do not apply here.

mercury-contaminated streams are collected and treated with sodium sulphide and then filtered. The streams consist of water used for washing the cells floors, hydrogen cooler

condensate, water used for backwashing the caustic filters, and brine leaks, laboratory effluent, washdown from the cell renewal area, and brine blowdown. The filrate is discharged into the sewer. Mercury levels are monitored in the sewer by an on-line Hg monitor. The filter cake (HgS) is treated with pH-adjusted hypochlorite. The mercury is dissolved, the solution is filtered to remove solids, and the filtrate is recycled back to the depleted brine circuit. The solids are mixed 40:60 with sand and deposited in a plastic-lined landfill site.

The hot, wet chlorine gas from the cells is cooled in an indirect cooler, passed through a mist eliminator, then through drying towers, another mist eliminator, compressors, and liquefiers. Condensate from the coolers and first mist eliminator is sent to a stripper. Steam and waste H_2SO_4 are added to the stripper to remove chlorine gas, which is recycled to the chlorine stream. The wastewaters from the stripper are sent to the sewer.

The uncondensed chlorine gas from the liquefaction stage and from returned tank cars is sent for muriatic production or scrubbed with sodium hydroxide to produce sodium hypochlorite. This hypochlorite is decomposed in the presence of an iron catalyst. The approximately 25% salt solution is discharged with the seawater used for cooling.

The hydrogen gas, as it leaves the decomposers, is saturated with mercury and water vapour. This gas is passed through individual primary coolers, a secondary cooler, compressor, demister, and a molecular sieve system. Part of the hydrogen gas is used for the manufacture of hydrochloric acid, and the rest is vented to the atmosphere. Condensate from the primary coolers returns to the decomposers. Condensate from the secondary cooler and demister is sent to the effluent treatment system.

The HCl generation units consist of a burner and two absorption towers in series. The tail gas then passes through a water scrubber and finally a caustic soda scrubber. Effluent from the first scrubber and cooling water is discharged directly to the treatment holding pond.

Caustic soda from the decomposer is filtered to remove impurities, cooled, and sent to storage. The caustic filter backwash goes to the effluent treatment system. Any caustic spills are recovered or treated in the effluent treatment system.

Boiler blowdown containing sulphates, phosphates, silica, iron and, carbonates is discharged to the holding pond.

All old pipes, pump casings, etc., are decontaminated, and then sent to the scrap yard.

Sanitary effluent goes to a septic tank and tile-field.

Runoff waters are collected and treated for mercury removal.

The cell room floor and trenches were reworked, and then coated with a sealant. In 1978-79 floors under the cell area were reconditioned and sealed to reduce mercury loss to ground. The old floor was removed, broken up, and the material was retorted for mercury recovery.

All liquid effluents from this plant, including the wastewaters treated to remove mercury, cooling water, process effluents not contaminated with mercury, and storm runoff are directed to a 24-hour holding pond. The net effect of the holding pond is not only a reduction in discharges of chlorine and suspended solids discharges but also a dampening effect on pH swings. Table 4 presents conventional pollutant concentrations and loadings for the sampled streams.

Plant No. 4

At Plant No. 4 calcium sulphate impurities from the rock salt as well as $CaCO_3$ and $Mg(OH)_2$, precipitated from the brine in the purification process, are flushed from the saturators and settle in a holding pit. Excess brine overflows to a second pit where it can be either recycled or pumped to a large unlined holding pond. The sludge in the pit is trucked to a dewatering area. The entrained brine, which contains around 2 to 5 mg/L Hg, and runoff from a collection sump in this area is pumped to the large holding pond. Periodically wastewater from the holding pond is syphoned to a smaller, lined treatment pond.

About 30 to 45 m^3/d of mercury-contaminated wastewaters from various sources flow to the brine pit from where they are transferred to the larger holding pond. The sources are: cell cleaning, floor washings, mercury treatment, hydrogen cooler condensate, hydrogen and vent line drains, brine leaks and drainage, caustic receiver drain, basement floor cleanup etc., which cannot be recycled directly to process or reused in process without further treatment, periodically wastewaters from this pond are transferred to a smaller, lined treatment pond.

The combined wastewaters in the lined treatment pond are first treated with sodium sulphite to destroy any free chlorine or sodium hypochlorite present. The pH is then adjusted to between 6 and 7, after which NaHS is added to precipitate HgS. Ferrous sulphate is added to consume any excess NaHS, which would otherwise have formed soluble mercury compounds after having formed the insoluble mercury sulphide. After settling, the relatively clear supernatant, which still contains about 0.3 mg/L Hg, is

TABLE 4 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 3, CHLOR-ALKALI-MERCURY CELL

Parameter	FINAL EFFLUENT				EFFLUENT TO POND				COOLING WATER (Intake)			
	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow (m^3/d)**		27736										
pH**	2632	7.6	3.1-9.9		1955	7.5	3.1-11.1		4	7.5	6.7-7.9	
Total Solids*	9	27560	21500-30600		3*	28567	25600-31100		3*	29333	26900-31100	
TDS	1	30200	-									
TSS	2610	2.0	0-31.9	0.35	6	6.0	3-9	1.03	185	106.5	0-3220	17.9
Conduct mh/cm	14	39286	32300-43800		5	39420	32300-44400		3	39533	36300-42800	
Dis. O_2	17	10.2	8.4-11.8									
Res. $C/_2$	2523	0.02	0-4.7	0.0035	1	0.1		0.017				
Hardness	6	4764	4070-5602		3	4795	4195-5668		3	4911	4092-6113	
Sulphate	5	1963	1770-2130	338	3	1994	1890-2100	343.5	3	1979	1820-2100	331.9
Sulphide	2529	0.10	0-1	0.017	4	0.5	0.5	0.086	2	0.5		0.084
H_2O_2	2503	0.13	0-3	0.022								
Dis. Ca	6	295.8	270-325	60.0	3	295.7	273-325	50.9	3	327.7	272-437	55.0
T. Cu	6	0.025	0.004-0.05	0.0043	1	0.003			3	0.028	0.003-0.04	0.0047
T. Fe	6	0.35	0.1-0.68	0.060	1	0.18			3	0.6	0.3-1	0.10
T. Pb	6	0.0013	0.001-0.003	0.0002	1	0.001			3	0.001		0.00017
Dis. Mg	6	978	825-1170	168.5	3	985.7	844-1180	169.8	3	994	828-1220	168.7
Dis. Hg	3	0.0009		0.00016					2	0.00007		
T. Hg	2612	0.003	0.0001-0.075	0.00052	8	0.020	0.0009-0.068	0.0034	81	0.00015	0.00005-0.0002	0.00007
T. Zn	5	0.035	0.005-0.08	0.0060	1	0.005			3	0.067	0.02-0.13	0.01

* The cooling water used is sea water.
** The units in the column headings do not apply here.

filtered through a sand filter. This treated effluent, which contains about 0.1 mg/L Hg, is combined with other mercury-free effluents and is sent through a flow meter and continuous sampler to the sewer.

The tail gas scrubber effluent (sodium hypochlorite), derived from filtered caustic, is decomposed in the presence of a nickel and iron chloride catalyst. The solution, mainly NaCl is then, with other wastewaters sent to the sewer.

Spent H_2SO_4 is partially used for pH control. The remainder is shipped to another plant for reuse.

Chlorine condensate is recycled to the brine circuit or discharged to the treatment pond depending upon the water balance.

The caustic filter backwash is dewatered. The wastewater goes to the mercury treatment circuit. The sludge is saved for retorting.

Neutral effluent streams, which are mercury-free, (e.g. cooling water, boiler blowdown, floor washings from clean areas, laboratory drains, water softener backwash, cooling tower blowdown, septic tank overflow) are discharged through the flow-measuring device without treatment.

Effluent streams which contain other chemicals but are essentially free of mercury are collected, partially neutralized, and discharged with other wastewaters from the plant. The effluent contains HCl storage overflow, drainage from the waste gas fans, floor drains - HCl and hypo areas, HCl burner cooling - including ejector water, truck and track scale house drainage, chlorine drying area drainage.

Surface waters and rainfall from outside the plant areas are drained away from developed areas. Storm runoff from most of the contaminated areas is collected and treated for mercury removal.

Data available on discharges of conventional pollutants from this plant are presented in Table 5.

Plant No. 5

At Plant No. 5, the underflow from the brine saturator and from the brine clarifier is discharged to a sloping cement pit and container respectively. These solids, plus entrained brine, are transported using a pay loader to a sludge dewatering area. The brine, which contains some soluble mercury, plus any runoff from this area, drains into an unlined pond. Periodically, wastewaters from this holding pond are pumped to a treatment pond.

TABLE 5 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 4, CHLOR-ALKALI-MERCURY CELL

	FINAL EFFLUENT			
Parameters	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow* (m^3/d)		620		
pH*	30	7.0	1.8-11.1	
Total Solids	6	7750	2200-12000	51.0
Suspended Solids	7	29	10-55	0-19
Hardness	28	240	130-775	
Chloride	7	4300	1500-7700	28.4
Sulphate	1	375		2.5
Total Res. Chlorine	1	70		
Fe	36	0.46	0.09-1.88	0.003
Cu	37	0.005	0.001-0.053	0.00003
Pb	31	0.004	0.001-0.040	0.00003
Zn	36	0.009	0.001-0.104	0.00006
Hg	300	0.041	0.02-0.20	0.00027
Cd		0.02		
Cr	1	0.01		
Co	1	0.02		
Mg	1	3.83		
Ni	1	0.08		
V	1	0.02		

* Units in the column headings do not apply here.

The combined wastewaters in the treatment pond are first treated with sodium thiosulphate to destroy any free chlorine or sodium hypochlorite. The pH is then adjusted to between 6 and 8.5, after which NaHS is added to precipitate HgS. Ferrous sulphate is added to consume any excess sodium hydrosulphide, which would otherwise have formed soluble mercury compounds after having formed the insoluble mercury sulphide. After three days of settling, samples are taken to ensure that the precipitated solids have properly settled. The clear supernatant is pumped into the sewer through a

flow-measuring weir and sampler. The mercuric sulphide sludge generated, is stored in three lined treatment ponds.

Deionizer wastes, once-through cooling water, laboratory drains, housekeeping wastewaters from non-contaminated areas join the septic tank overflow and are discharged separately via a flow-measuring device and sampler.

The effluent (hypochlorite) from the tail gas scrubber is discharged to a nearby pulp and paper company's effluent treatment facility.

Spent H_2SO_4 is transferred to another plant for reuse or used in-plant for pH control.

Chlorine condensate and hydrogen cooler condensate are recycled to the brine circuit.

Caustic filter backwash is dewatered and recycled to the caustic circuit. The mercury sludge is stored on-site in plastic drums for future mercury recovery.

Storm runoff, cooling tower blowdown, and any brine tank overflow are collected in a retention ditch. If the mercury content of these wastewaters is high, the effluent is pumped to the treatment pond. If not, the wastewaters are mixed with the treated effluent and discharged through the flow-measuring weir and sampler.

Data available on discharges of conventional pollutants from this plant are presented in Table 6.

2.4 Priority Pollutants* and Biological Testing - Methodology

2.4.1 Priority Pollutants. The Environmental Protection Agency in the United States of America established the presence of some of the 129 listed priority pollutants (see Table 1, Appendix A) in mercury cell plants, by screening and verification sampling programs. A summary of the data they collected is shown in Table 7. No toxic organics at significant levels were found.

> The term "significant concentration" by EPA terminology means an observed concentration in any 24- or 72-hour composite sample that is above the analytical detection limit, and treatable by an available technology regardless of economic considerations.

In Canada, the occurrence of any of the 129 listed priority pollutants in final effluents from mercury cell plants was tested by sampling three of the five operating

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* For priority pollutants, as used in this report, refer to the EPA list shown in Appendix A.

TABLE 6 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 5, CHLOR-ALKALI-MERCURY CELL

	INTAKE WATER		COOLING WATER		TREATED EFFLUENT			
Parameter	No. of Values	Avg. Conc'n (mg/L)	No. of Values	Avg. Conc'n (mg/L)	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow (m^3/d)*	1					460		
pH*	1	6.8	1	6.6	15	5.5	2.7-13.2	
Total Solids	1	100	1	170	15	30200	4300-63700	230
Susp. Solids	1	< 5	1	< 5	16	41	3-120	0.3
Chloride	1	12	1	44	1	9200		70.5
Sodium	1	11	1	41	1	12700		97.3
Sulphate	1	19	1	14	1	7900		60.5
Calcium	1	5	1	8	1	131		1.0
Magnesium	1	1.2	1	1.6	16	2.4	1.1-3.2	0.02
TOC	1	6		-	1	235		
Sulphide		-	1	< 0.15	1	< 0.15		
Zinc		-		-	16	0.05	0.002-0.21	0.0004
Copper		-		-	16	0.07	0.002-0.65	0.0005
Iron		-		-	15	0.65	0.21-2.2	0.005
Lead		-		-	12	0.006	0.002-0.011	0.00005
PO_4		-		-	1	0.46		0.003
Mercury	1	0.002	1	0.057	90	0.035	0.007-0.049	0.00027
Cr					1	0.23		
Li					1	0.07		

* The units in the column heading do not apply here.

TABLE 7 CONCENTRATIONS OF TOXIC POLLUTANTS OBTAINED THROUGH VERIFICATION SAMPLING OF EFFLUENT AT USA PLANTS[1]

SUBCATEGORY	CHLORINE (MERCURY CELL)					
	CONCENTRATIONS (mg/L) IN PLANT EFFLUENT					
Pollutant / Plant	No. 299	No. 747	No. 317	No. 106	No. 167	Avg.
Antimony	0.15	<0.25	<0.25	<0.45	<0.65	<0.23
Arsenic	0.063	<0.010	0.020	<0.005	0.38	<0.096
Cadmium	0.073	0.120	<0.025	0.016	0.010	<0.050
Chromium	<0.06	<0.05	<0.05	<0.01	<0.050	<0.044
Copper	0.038	<0.025	<0.030	0.043	<0.025	<0.033
Lead	<0.050	0.073	0.170	0.38	0.12	<0.16
Mercury	0.029	0.10	0.19	<0.0005	0.32	<0.13
Nickel	<0.050	<0.050	<0.067	0.140	<0.050	<0.074
Silver	<0.015	<0.015	<0.015	0.260	<0.105	<0.067
Thallium	0.20	<0.045	<0.25	0.26	0.090	<0.17
Zinc	0.100	<0.025	0.510	0.088	<0.025	<0.15

	CHLORINE WASTE LOAD (kg/kkg)					
Plant	No. 207	No. 014	No. 819	No. 747	No. 106	No. 589
Residual Chlorine	0.33	0.04	Non detected	0.002	0.001	0.003

Note: The results of analysis of treated effluent represents plant performance observed during three days of sampling. The data for toxic pollutants found above treatable concentrations in raw wastes are summarized above. Data are presented from four plants practicing BPT technology (sulfide precipitation followed by filtration). Sampling data for a fifth plant, No. 299, reflect the quality of effluent prior to filtration.

plants, using the "Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations", published in the U.S. Federal Register, dated December 3, 1979.[2] Information was derived from the chemical analysis and flow measurements of representative final effluents from these plants.

i) Metals

Twenty-four-hour composite samples of final effluents were collected during the 1981 survey, as well as during monitoring surveys carried out over the past five years by governmental agencies and by company personnel.

Metal analyses are readily determined by atomic absorption spectroscopy or by an inductively coupled argon plasma optical emission spectrophotometer. Mercury is normally determined by the automated cold-vapour technique. The priority metals found in the final effluents of a mercury cell plant are shown in Table 8.

ii) Organic Pollutants

Twenty-four-hour composite samples of the plant intake water and final effluent were collected for each day of the survey (normally a three-day survey) for each of the three plants monitored. These samples were cooled to 4°C as quickly as possible and then shipped to the EPS River Road Laboratory, Ottawa. Upon arrival at the laboratory, the samples were extracted using standard procedures and then stored at 2 to 4°C until analyzed.

At the River Road Laboratory the volatile organic fractions were subjected to the purge-and-trap procedure followed by a gas chromatograph using a packed column. The concentrations were quantified by comparison with standards.

The base, neutral, and acid fractions were analyzed using liquid/liquid extraction procedures followed by analysis with a gas chromatograph equipped with a high-resolution capilliary column. This column is considered superior to the packed column specified in the methods. The base-neutral fractions were quantified using standards and confirmed using a mass spectrometer coupled to a data system library containing over 30,000 compounds. The levels of priority organic pollutants found in the final effluent from mercury cell plants are shown in Table 9.

2.4.2 Aquatic Toxicity Testing. At one plant a large 24-hour composite sample of the final effluent was collected for acute lethality testing. Toxicity testing methods are

TABLE 8 SUMMARY OF FINAL EFFLUENT PRIORITY METAL CONCENTRATIONS AND LOADINGS AT MERCURY CELL PLANTS

Pollutant	Concentrations (mg/L)		Daily Loadings (kg/day)		Unit Loadings (kg/kkg)		Proposed EPA Criteria[1] (24 hr. average)		
	Average	Maximum	Average	Maximum	Average	Maximum	Freshwater aquatic life (ug/L)	Saltwater aquatic life (ug/L)	Human Health (ug/L)
Cadmium	<0.01	<0.01	<0.006	<0.010	<0.00004	<0.00005	0.012 (hardness of 50)	4.5	10
Chromium	<0.03	<0.05	<0.06	<0.60	<0.0008	<0.004	0.29 (hexavalent)	18	50 (hexavalent)
Copper	0.029	0.06	0.45	1.32	0.0023	0.006	5.6	4.0	No data
Lead	0.005	0.010	0.058	0.20	0.00027	0.0010	0.75 (hardness of 50)	25 (chronic)	50
Mercury	0.023	0.041	0.066	0.11	0.00042	0.0006	0.00057	0.025	0.144
Nickel	0.015	0.02	0.130	0.22	0.00070	0.0014	56	7.1	13.4
Zinc	0.063	0.15	0.41	1.22	0.0025	0.007	47	58	No data

1 From EPA "Ambient Water Quality Criteria" Reports.

TABLE 9 PRIORITY ORGANIC POLLUTANTS FOUND IN MERCURY CELL CHLOR-ALKALI PLANTS FINAL EFFLUENT, THEIR CONCENTRATION RANGE AND AMBIENT WATER QUALITY CRITERIA PROPOSED BY EPA (USA)

Parameter	Levels found in C-A Effluent (ug/L)	Proposed EPA Criteria[1]				
		Freshwater Aquatic Life (ug/L)		Saltwater Aquatic Life (ug/L)		Human Health
		Acute	Chronic	Acute	Chronic	Estimated
Chloroform	T-410	28 900	1 240	-	-	
Carbon Tetrachloride	T-24	35 200	-	50 000	-	
1,2-Dichloroethane	T-12	118 000	20 000	113 000	-	
Trichloroethylene	T-72	45 000	-	2 000	-	
Bromodichloromethane	T-28	11 000	-	12 000	6 400	
2,4,6-Trichlorophenol	T-6	6 040	970	-	-	
2-Nitrophenol	T-1	230	-	4 850	-	
4-Chloro-m-cresol	T-3	30	-	-	-	3 000
Toluene	T-2	17 500	-	6 300	5 000	14.3
1,1-Dichloroethene	T-18	11 600	-	22 400	-	
1,1,1-Trichloroethane	T-94	18 000	9 400	31 200	-	18.4
1,2-Dichloropropane	T	23 000	5 700	10 300	3 040	
Trans-1,3-Dichloropropene and cis	T-4	6 060	244	790	-	87
1,1,2-Trichloroethane	T-14	18 000	9 400	31 200	-	
Dichloromethane	T-55	224 000	-	-	-	
Diethylphthalate	T-3	52 100	-	7 590	-	350 mg/L
Dibutylphthalate	T-16	940	-	-	-	34 mg/L
Di(2 ethylhexyl)phthalate	T-4	11 100	< 3	-	-	15 mg/L
1,1-Dichloroethane	T	No data				
Trans-1,2-Dichloroethylene	0-23	11 600	-	224 000	-	
Ethylbenzene	T-1	32 000	-	430	-	1.4 mg/L
1,4-Dichlorobenzene	0-9	1 120	763	1 970	-	400 ug/L
Phenol	0-1	10 200	2 560	5 800	-	3.5 mg/L

1. From EPA "Ambient Water Quality Criteria" Reports.
T = Trace

available for evaluating the effects of chemical substances on aquatic life. The two most commonly applied tests are:

1. Acute Lethality Tests

Acute lethality tests are generally considered to provide rapid and reproducible concentration-response curves for identifying and estimating the effects of chemicals on aquatic organisms. These tests provide the most practical means for evaluating:

a) the relative toxicity of a number of chemicals;
b) the upper limit of the range of concentrations producing toxic effects;
c) the relative sensitivity of different aquatic organisms to that chemical;
d) the effects of water quality on toxicity of chemicals;

and for developing a knowledge about the concentration-response relationship and the significance of the duration of exposure on toxicity.

The general limitations of acute lethality tests in evaluating toxicity are that the results of such tests usually do not provide information on sublethal or cumulative effects.

2. Chronic Tests

Chronic tests measuring effects of chemical exposure on the reproductive process are useful because the empirical observations represent a total effect of all important sublethal effects; e.g., assimilation, metabolism, etc. on life processes such as growth, reproduction, respiration, etc.

The results of such studies, which usually involve exposure over a complete life cycle of the test populations, provide empirical information on the effects of chronic exposure on the species in question, identify those chemicals which may be cumulatively toxic, allow one to estimate chronically safe concentrations for closely related species, and are useful in deriving water quality criteria for the protection of aquatic life.

The Environmental Protection Agency derived water quality criteria for a large number of chemicals tested individually. Acute and chronic tests were carried out for both fresh water and saltwater aquatic life. The values found pertaining to the organic chemicals found in mercury cell plant effluent are shown in Table 9.

Normally chemical plant effluents contain a variety of classes of chemicals at a range of concentrations. A major consideration in the environmental testing of complex chemical mixtures is that such mixtures are potentially capable of causing additive, antagonistic or synergistic responses in test organisms.

In addition to collecting samples for chemical analysis and aquatic toxicity testing, five-gallon 24-hour composite samples of the final effluent, for each of two plants monitored, were collected and shipped to the B.C. Cancer Research Centre in Vancouver for testing for potential genotoxic activity.

2.4.3 Biological Testing. To establish with absolute certainty the degree of hazard posed by a particular material would require testing of all potential target organisms for their various responses. In light of the large number of complex mixtures entering the environment, it is readily apparent that the costs, both of time and money in making such an assessment would be staggering. On the other hand, predictions concerning potential hazards based on the response of a single species to a chemical mixture have an unacceptably low level of certainty or dependability.

One method of increasing the level of confidence is to use a series of tests and develop a hazard estimate based on pooled results from these systems. This group of systems would ideally attempt to represent as broad a spectrum as possible.

Several in vitro short-term bioassays are available for the prescreening of chemicals for potential carcinogenic activity. The tests chosen for this study included the following:

Each straight effluent sample was tested for mutagenic activity using the Salmonella mutagenicity test (Ames test).

The extract from each effluent was prepared[5] and tested for the mutagenic potential by assaying for the capacity:

(i) to induce mutations in Salmonella typhimurium (Salmonella mutagenicity test);
(ii) to induce chromosome abnormalities in cultured Chinese hamster ovary (CHO) cells (chromosome aberration test);
(iii) to inflict damage to DNA of cultured human fibroblasts (DNA repair test);
(iv) to inhibit repair of DNA damage in cultured human fibroblasts (DNA repair inhibition test).

In vitro cytotoxicity testing is still in its infancy, especially as applied to complex environmental components. These tests with bacterial mutagenicity assays are not considered to be so authoritative as epidemiological data or long-term whole animal studies. For this reason, short-term tests are not used to provide definitive evidence about the hazards of a chemical. Rather, they are considered to be suggestive evidence of a chemical's potential to cause genotoxic effects. A positive Ames test does not necessarily show that a compound is carcinogenic, whereas a negative result does not rule

out that possibility. Over-interpretation at this stage of research, especially with respect to relative hazard or negative results, should be avoided. As a prescreen to aid the investigators in ordering their priorities, however, short-term testing appears to be a valid testing approach.

For more detail on the materials and methods used in this study one is referred to the report "Biological Testing of Industrial and Municipal Effluents for Genotoxic Activity".[5]

2.5 Discussion of Results

2.5.1 Conventional Pollutants. The results shown in Tables 2 through 6 indicate that control of pH, suspended solids, and residual chlorine in the final effluent discharged from mercury cell plants has to be more consistent.

Normally the pH of the final effluent is within the range of 6 to 9, however, pH ranges between 2 to 12 do occur. At one plant, where the effluent is retained for 24 hours, the pH range does not vary widely.

The concentration of suspended solids from these plants is normally low; i.e., less than 25 mg/L, because the brine treatment solids are removed to secure land fill sites, and the process effluents are usually filtered after sulphide treatment for mercury removal. Excursions do occur, however, when equipment not contaminated with mercury is cleaned, or when boiler or cooling tower blowdown is discharged without settling or filtration.

Residual chlorine levels in the final effluent from most of these plants is normally zero, but can range from zero to very high levels (100 ppm). Because of the environmental effects of high levels of chlorine in wastewater discharges*, dechlorination treatment should be practiced. Chlorine residuals remaining after the recovery, or decomposition, or both and recycling steps noted in Section 2.3.2, would be amenable to treatment with reducing agents such as sulphur dioxide or hydrogen peroxide.

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*Note: The acute toxicity to fish of free chlorine and inorganic chloramines, as determined by 96-hr continuous exposure at constant concentrations, differs considerably among species, among individuals of different sizes, and among different stages of life history. For example adult salmonids may live indefinitely at concentrations near 0.050 mg/L, whereas the LC_{50} values for fry and very small juveniles are close to 0.050 mg/L. Chronic effects on growth and other responses of salmonids may occur at concentrations near 0.020 mg/L or even lower. Threshold concentrations of inorganic chloramines have effects on the growth of salmonid alevins and juveniles somewhere between 0.010 and 0.020 mg/L of total residual chlorine. Thus the difference between acutely toxic and chronically toxic concentrations of inorganic chloramines is very great for some species. ("Toxicity of Residual Chlorine Compounds to Aquatic Organisms", EPA 600/3-78-023.)

2.5.2 Priority Pollutants and Biological Testing

i) Metals

Mercury is the toxic metal of major concern in the production of chlorine by the mercury cell process. The amount of mercury a plant is allowed to discharge is controlled under the "Chlor-Alkali Mercury Liquid Effluent Regulations".[3]

All metal concentration levels are very low (see Table 8), even though the amount of metals found to be discharged with the final effluent includes both the background contribution (plant intake flow times the concentration) and the contribution for the plant itself. By applying best practical control technology (sulphide precipitation followed by filtration) for the removal of mercury, effective control of other metals from within the plant is also assured. At some plants the zinc and chromium levels might be a little higher due to the discharge of untreated cooling tower blowdown.

ii) Organic Pollutants

Even by taking into account the possibility of antagonistic or synergistic effects of the priority organic pollutants found in mercury cell chlor-alkali plant effluent, one would not likely classify these effluents as being hazardous to aquatic life, since the concentrations of the organic pollutants found are so very much lower than the ambient water quality criteria set for acute and chronic toxicity (Table 9).

iii) Aquatic Bioassay

Normally bioassay testing of chlor-alkali plant final effluent shows 100 percent survival in 100 percent effluent over a 96-hour period. If the effluent is toxic, the reason lies usually in high levels of residual chlorine or a pH range outside 6 to 9.

iv) Biological Testing

Three final effluent samples from mercury cell chlor-alkali plants were tested for genotoxic activity using a battery of four short-term bioassays. Each straight effluent was tested for mutagenicity in Salmonella typhimurium using a suspension test procedure. The concentrated extracts, prepared from the three effluent samples, were tested for their capacity to induce mutatations in Salmonella typhimurium, chromosome aberrations in Chinese hamster ovary cells, DNA damage, and inhibition of DNA repair in cultured human fibroblasts.

No mutagenic activity was demonstrable with any of the three straight effluents in the Salmonella mutagenicity test over the dose range tested. Mutagenic

activity was detected in one of the three effluent extracts using the Salmonella mutagenicity test. This extract yielded a four-fold increase in strain TA 100 with and without the liver-enzyme-activation system (S-9). No mutagenic activity was demonstrable with the other two effluent extracts or the extract blank of whether S-9 was included or not.*

The three effluent extracts caused damage to chromosomes in the ovary cells of Chinese hamsters. Two extracts elicited chromosome aberrations only in the presence of S-9. With the addition of S-9, the other extract sample caused no chromosomal damage. The data indicate that the chromosome-damaging activity of the effluent extracts was demonstrable over a very narrow dose range.

No DNA repair was demonstable in cultured human fibroblasts for the three sample extracts.

Two of the three extracts exhibited DNA repair inhibition. The addition of S-9 eliminated the inhibitory effect in one of these samples.

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*Note:

The Salmonella-microsome test was developed by Dr. Bruce Ames, a biochemist at the University of California in the early 1970's. The test measures the mutagenic potential of a chemical to produce genetic changes.

In the Ames test, bacteria and the chemical are put together in a petri dish and incubated. If the chemical being tested is a mutagen; it will mutate the bacteria which would be difficult to detect. Thus, reverse mutation is used. Ames and his colleagues have developed bacteria that already have mutations in the genes that govern the ability to make histidine which fosters bacterial growth.

If the chemical being tested is a mutagen and if it acts on the bacteria, the already mutated bacteria are mutated again. As a result, the bacteria makes histidine and begins to grow. The colonies are visible after 48 hours.

Currently five strains are normally employed in the test: TA 98, TA 100, TA 1535, TA 1537 and TA 1538. Strains TA 98, TA 1537, and TA 1538 carry frameshift mutations and therefore are reverted by agents that will produce new frameshifts. Strains TA 100 and TA 1535 carry missense mutations and are reverted by agents that cause base-pair substitutions, although it has been observed that strain TA 100 also will respond to some frameshift mutations. (See the Glossary for the definition of terms).

In 1975, it was shown that 90 percent of the known carcinogens tested were mutagenic in the Ames test. This high correlation was made possible by the discovery that many carcinogens are not active as such, but are metabolized to the active form by enzymes in the liver and other organs. This mammalian metabolic system could be duplicated in the microbial mutagenicity assays by incorporating into the test system an extract from the liver of a rat, (S9). The liver enzymes converted the carcinogens to their active forms, which were detected as mutagens by the bacteria. The high correlation between carcinogenic and mutagenic activity has also been found using other short-term mutagenicity assay procedures.[6]

In the solvent control, dimethyl sulphoxide (DMSO) at a final concentration of 5 and 10 percent occasionally elicited DNA repair inhibition. The same was observed with the top two dilutions of the extract blank. Therefore, in assessing the inhibitory effect exerted by an effluent extract, the top two dilutions (1:10 and 1:20) were not considered.

The results of this study are summarized in Tables 10 and 11. For more details, refer to Tables B1 to B10 in Appendix B.

TABLE 10 SUMMARY OF TESTING OF EFFLUENT SAMPLES

Effluent Code No.	STRAIGHT EFFLUENT		EXTRACT							
	Salmonella Mutagenicity		Salmonella Mutagenicity[a]		Chromosome Aberration[b]		DNA Repair[c]		DNA Repair Inhibition[d]	
		+S-9		+S-9		+S-9		+S-9		+S-9
1	-	-	+[e]	+[e]	-	+	-	-	+	-
2	-	-	-	-	-	±	-	-	+	+
3	-	-	-	-	+	-	-	-	-	-
Extract Blank				-	-	-	see page 35		-	-

[a]Salmonella mutagenicity:
+ = positive: colony count reaching at least twofold increase above background.
± = dose-related increase in colony count but not reaching twofold above background.
- = negative: neither dose-related nor twofold increase in colony count above background.

[b]Percentage of metaphases with chromosome aberrations: - = 0-4%; ± = 5-9%; + = ≥10%.

[c]Maximum mean grains per nucleus observed: - = 0.4; ± = 5-9; + = ≥10.

[d]DNA repair inhibition: + = inhibition observed; - = inhibition not observed.

[e]Only in TA100.

2.5.3 Discussion. Human beings and the environment are being exposed each year to a large number of chemical substances and mixtures, and some of these may present an unreasonable risk of injury to health. Many of these compounds are mutagenic to lower organisms, and there are sound biological reasons to conclude that at least some are also mutagenic to man.

TABLE 11 SUMMARY OF SALMONELLA MUTAGENICITY TEST RESULTS

Effluent Code No.	STRAIGHT EFFLUENT								EXTRACT	
	1535 +S-9	100 +S-9	1537 +S-9	1538 +S-9	98 +S-9	1535 +S-9	100 +S-9	1537 +S-9	1538 +S-9	98 +S-9
1	- -	- -	- -	- -	- -	- -	+4 +4	- -	- -	- -
2	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
3	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
Extract Blank						- -	- -	- -	- -	- -

+ = positive: colony count reaching at least twofold increase above background. Number indicates fold increase in mutant colony count above background.

± = dose-related increase in colony count but not reaching twofold above background.

- = negative: neither dose-related nor twofold increase in colony count above background.

During the past few years genetic effects have occupied a prominent place in human toxicology and ecotoxicology. Extensive studies have been devoted to the development of sensitive short-term tests for identifying chemicals that induce mutations. In many cases, mutagens do prove to be carcinogens, however, care should be taken not to refer to compounds as being carcinogenic on the outcome of a mutagenicity test alone.

To make efficient use of research facilities and funds, testing and evaluation of chemicals should be based on the principles of stepwise progression. This study, which is at the screening level, is designed to provide the information required for the identification of potential hazards. At this level, studies include obtaining values from the literature on biodegradability, potential of bioaccumulation, and other fate processes (see Table 15), carrying out testing for toxicity, and performing four short-term tests for mutagenicity.

Based on these results a decision will be taken as to whether higher levels of testing (e.g. more accurate assessment of environmental hazards through animal studies) are required. If animal studies prove to be negative, they would supercede the results of the mutagenicity tests as far as carcinogenic activity is concerned. The ultimate in determination of carcinogenicity is, of course, on humans, and where adequate epidemiological data are available, they would supercede the data from animal

carcinogenicity studies. Other factors that will be taken into consideration, when setting priorities, are volumes produced, likelihood of human exposure, anticipated toxicity, and environmental distribution.

The ultimate objective of carrying out tests in ecotoxicology, as in human toxicology, is to establish protective measures against the harmful effects of environmental pollutants on the various constituents of ecosystems. To this end the risks need to be disclosed first.

In this respect, it must be emphasized that our knowledge both qualitatively and particularly quantitatively is very limited. The available information is primarily composed of the results from studies of acute and chronic toxicity in (Tables 9) as well as mutagenicity and carcinogenicity studies (Table 13). The criteria estimated for human health (Table 9) are based on inhalation and ingestion from water, since humans are exposed to any of three primary routes: inhalation, intake of water or other fluids, and ingestion of foods.

Even for occupational carcinogenesis there is generally believed to be a dose-response relationship. The existence of dose-response relationships does not contradict the concept that thresholds do not exist for the occurrence of cancer following exposure to carcinogenic agents. The fact that it may be very difficult to obtain definitive information on the incidence of cancer at very low levels of exposure provides a background for our uncertainty in this area. Adding to this uncertainty is the fact that adequate methods for sampling and analysis are still being evaluated in Canada. We should nevertheless attempt to obtain as much information as possible on the levels of risk due to low-level exposure. Whether low levels of risk are acceptable is then a matter for evaluation, not only by scientist, but by industry and other experts from all relevant disciplines. This group, however, should bear in mind that certain priority contaminants are retained in living organisms due to their physio-chemical nature and due to their hampered elimination because of their harmful effect on excretory organs. The cumulative absorption of small doses of pollutants brings about disorders at the level of the receptors when, after a certain time, toxic concentration thresholds have been reached.

Analysis has shown that as many as 700 organic chemicals can be present in drinking water supplies; among these chemicals many suspect carcinogenic and mutagenic contaminants may be present.[7,8,9] Short-term mutagenicity tests, which have been used not only for assessing carcinogenic potential in complex environmental samples but also for checking drinking water supplies, industrial effluents, and sanitary effluents, showed

TABLE 12 KEY TO ABBREVIATIONS USED IN TABLE 13

bdw - wild bird species
brd - bird (domestic or lab)
CAR - carcinogenic effects
cat - cat
chd - child
ckn - chicken
cns - central nervous system effects
ctl - cattle
dck - duck
dog - dog
dom - domestic
EPA - Environmental Protection Agency
ETA - equivocal tumorigenic agent
eye - administration into eye (irritant)
frg - frog
g or gm - gram
gpg - guinea pig
grb - gerbil
ham - hamster
hmn - human
ial - intraaural
IARC - International Agency for Research on Cancer
iat - intraarterial
ice - intracerebral
icv - intracervical
idr - intradermal
idu - intraduodenal
ihl - inhalation
imm - immersion
imp - implant
ims - intramuscular
inf - infant
ipc - intraplacental
ipl - intrapleural
ipr - intraperitoneal
irn - intrarenal
isp - intraspinal
itr - intratracheal
ivg - intravaginal
ivn - intravenous
LC50 - lethal concentration 50 percent kill
LCLo - lowest published lethal concentration
LD50 - lethal dose 50 percent kill
mam - mammal (species unspecified)
man - man
mg - milligram (10^{-3} gram)
mky - monkey
mul - multiple routes
mus - mouse
MUT - in vivo mutagenic effects
NEO - neoplastic effects
ocu - ocular
open - open irritation test
orl - oral
OSHA - Occupational Safety and Health Administration
par - parenteral
pgn - pigeon
pig - pig
preg - pregnant
qal - quail
rat - rat
rbt - rabbit
rec - rectal
scu - subcutaneous
sql - squirrel
TCLO - lowest published toxic concentration
TER - teratogenic effects
TFX - toxic effects
trk - turkey
ug - microgram (10^{-6} gram)
unk - unreported
UNS - toxic effects unspecified in source
wmn - woman

TABLE 13 POTENTIAL INDUSTRIAL CARCINOGENS AND MUTAGENS IN MERCURY CELL CHLOR-ALKALI FINAL EFFLUENT

PARAMETER	HUMAN TOXICITY DATA[1]							
	TOXICOLOGY[1]	CARCINOGEN[1]	TCLo	TFX	ADM	TERATOGEN[1]	MUTAGENICITY[2]	
4-Chloro-m-cresol	orl-rat LDLo: 500 mg/kg scu-rat LD50: 400 mg/kg ipr-mus LDLo: 30 mg/kg scu-mus LDLo: 200 mg/kg						S. typhimurium strains in which mutagenic activity observed	Mammalian Metabolic Activation
Chloroform	LDLo: 40 mg/kg, orl-hmn TCLo: 100 ppm/7H/(6-15 D preg) LD50: 704 mg/kg, scu-mus	TDLo: 70 gm/kg/78 WI TFX: NEO, orl-rat 18 gm/kg/120 DI: CAR orl-mus (animal carcinogen orl)	10 ppm/1Y	SYS	ihl	TCLo: 100 ppm/7H (6-15 D preg) TFX: TER, ihl-rat		
1,2-Dichloropropane	LDLo: 50 mg/kg, orl-hmn Dermatitis, liver, kidney and minor heart damage in animals exposed to high concentration						TA 100, TA 1535 TA 1978	+ -
Trichloroethylene	LDLo: 50 mg/kg, orl-hmn LDLo: 857 mg/kg, orl-hmn TCLo: 6900 mg/m^3/10M, TFX: CNS, ihl-man Narcotic and anesthetic in high concen. Additive, Fatalities due to heart failure	TDLo: 351 gm/kg/78 WI TFX: CAR, orl-mus	160 ppm/83M	CNS	ihl		TA 100 TA 1535, TA 1538	+ Mouse, B6C3F$_1$ -
1,1,2-Trichloroethane	LDLo: 50 mg/kg, orl-hmn Narcotic; irr to eyes, nose and lungs; injurious to liver and kidneys LD50: 227 mg/kg, scu-mus LDLo: 95 mg/kg, inv-dog LDLo: 500 mg/kg, scu-rbt	Suspect[2] (mouse liver)					With TA 100 tester strain** (in desiccator) found to be negative	-
1,1-Dichloroethylene	TCLo: 25 ppm TFX: SYS, ihl-hmm LDLo: 225 mg/kg, ivn-dog LDLo: 3700 mg/kg, scu-rbt	Experimental carcinogen 3) 1088					+ (Strain not ** identified)	-
1,2-Dichloroethane	LDLo: 500 mg/kg, orl-hmn LDLo: 810 mg/kg, orl-man Experimental mutagen and teratogen 3) 658 LDLo: 600 mg/kg, ipr-rat LDLo: 500 mg/kg, scu-rat	Experimental carcinogen 3) 658	LDLo: 845 mg/kg		orl	Experimental teratogen 3) 658	TA 100[c], TA 1530, TA 1535[c] - TA 1535 + c = activity observed but no positive dose - response demonstrated Weak mutagen in S. typhimurium TA 1530, TA 1535 and TA 100 tester strains (when in agar or desiccator) and negative when tested at 125 mg/plate with S-9 activation in TA 1538 and TA 98**	

TABLE 13 POTENTIAL INDUSTRIAL CARCINOGENS AND MUTAGENS IN MERCURY CELL CHLOR-ALKALI FINAL EFFLUENT (CONT'D)

PARAMETER	TOXICOLOGY[1]	HUMAN TOXICITY DATA[1]				
		CARCINOGEN[1]	TCLo	TFX	ADM	TERATOGEN[1]	MUTAGENICITY[2]
Toluene	LDLo: 50 mg/kg, orl-hmn TCLo: 200 ppm TFX: CNS, ihl-hmn LD50: 5300 ppm, ihl-mus						
1,1,1-Trichloroethane	LDLo: 500 mg/kg, orl-hmn TCLo: 350 ppm TFX: PSY, ihl-man TCLo: 920 ppm/70M, TFX: CNS, ihl-hmn LCLo: 27 000 mg/m^3/10M, ihl-man						TA 100 +
Bromodichloromethane	Acutely toxic to mice * orl-rat LD50: 916 mg/kg, orl-mouse LD50: 450 mg/kg	Carcinogenic in mice (significance of test results open to question)					Positive when tested in desiccator but not when incorporated into agar when tested with S. typhimurium TA 100
1,4-Dichlorobenzene	TDLo: 300 TFX: UNS, orl-hmn LD50: 2500 mg/kg, ipr-rat	TDLo: 142 mg/kg/1, TFX: CAR, scu-mus - in rat pulmonary cells suspect carcinogen					Mitotic anomalies in cells and somatic chromosomes of treated root tips of Vicia faba
Ethylbenzene	TCLo: 100 ppm/4H, ihl-hmn	No data					
1,1-Dichloroethane	Cat-kidney damage Dog-liver injury Rat-retarded fetal development					No data	No data Salmonella -
Trans-1,2-Dichloro-ethylene	TCLo: 4800 mg/m^3/10M TFX: CNS, ihl-hmn	No data					E. Coli -
Phenol	LDLo: 140 mg/kg, orl-hmn LD50: 250 mg/kg, ipr-rat LDLo: 650 mg/kg, scu-rat LD50: 344 mg/kg, scu-mus LDLo: 80 mg/kg, scu-cat	TDLo: 4000 mg/kg/20 WI TFX: CAR, skn-mus Data inappropriate and inadequate for judging whether phenol to be a carcinogen in ingested water					Back mutations in E. Coli Non-mutagenic in Neurospora Mutagenic in Drosophila
2-Nitrophenol	Liver and kidney damage in experimental animals LDLo: 100 mg/kg, ivn-dog						
2,4,6-Trichlorophenol	LDLo: 500 mg/kg, orl-hmn LD50: 276 mg/kg, ipr-rat	TDLo: 29 gm/kg, 78 WI TFX: CAR + in male F344 rats + in both sexes of B6C3F$_1$ mice					Negative using Salmonella microsome test with non-activated and activated systems
Dichloromethane	LD50: 500 mg/kg, orl-hmn LD50: 1500 mg/kg, ipr-mus LD50: 6460 mg/kg, scu-mus LD$_{100}$: 950 mg/kg, ipr-dog LDLo: 2700 mg/kg, scu-dog LDLo: 200 mg/kg, ivn-dog LDLo: 2700 mg/kg, scu-rbt	Carcinogenic response in mice, but significance of results open to question	500 ppm/1Y I LDLo: 500 mg/kg, orl	CNS	ihl		Mutagenic properties in S. typhimurium TA 100 and in immunity-suppressed mice

TABLE 13 POTENTIAL INDUSTRIAL CARCINOGENS AND MUTAGENS IN MERCURY CELL CHLOR-ALKALI FINAL EFFLUENT (CONT'D)

PARAMETER	HUMAN TOXICITY DATA[1]						
	TOXICOLOGY[1]	CARCINOGEN[1]	TCLo	TFX	ADM	TERATOGEN[1]	MUTAGENICITY[2]
Toluene	LDLo: 50 mg/kg, orl-hmn TCLo: 200 ppm TFX: CNS, ihl-hmn TLCo: 100 ppm TFX: PSY, ihl-man LC50: 5300 ppm, ihl-mus						
Carbon Tetrachloride	LCLo: 1000 ppm, ihl-hmn TCLo: 20 ppm TFX: CNS, ihl-hmn LCLo: 43 mg/kgm/orl-hmn TDLo: 1800 mg/kg, TFX: SYS and PUL orl-wmn TDLo: 1700 mg/kg TFX: CNS, orl-man Narcotic; death results due to respiratory failure; in case that recover, serious kidney, liver and lung damage occurs; lower doses produce severe gastro-intestinal upset, kidney and hepatic damage	TDLo: 4800 mg/kg/88 DI, TFX: CAR, orl-mus TDLo: 133 gm/kg/25 WI, TFX: NEO, scu-rat TDLo: 3680 mg/kg/30 WI, TFX: CAR, orl-ham TDLo: 159 gm/kg/25 WI, TFX: CAR, scu-rat TDLo: 159 gm/kg/20 WI, TFX: CAR, rec-mus TDLo: 120 mg/kg/88 DI, TFX: CAR, orl-mus				TCLo: 300 ppm (6-15D preg) TFX: TER, ihl-rat	

1 Potentially Toxic and Hazardous substances in the Industrial Organic chemicals and Organic Dyes and Pigment Industries PB 80-180482
2 Aquatic Pollutants: Transformation and Biological Effects, Pergemon Press
* From NIH-EP Chemical Information System
** Potential Industrial Carcinogens and Mutagens, Lawrence Fishbein, Elsevier*
+ Activity in presence of S-9 microsome fraction from liver of rats unless species otherwise specified. Animals pretreated with Aroclor 1254 to induce microsomal enzymes unless other inducing agents specified.
- Activity in absence of S-9 microsome fraction.
± Activity both in presence and absence of S-9 microsome fraction.

that the drinking water from numerous sources exhibits some mutagenic activity.[10,11] Many of the compounds present in the drinking waters were the same as those found in the survey of chlor-alkali plant effluents and in the same concentration range.

The genotoxic activity observed in the chlor-alkali plants effluent and wastewater concentrates, which contained a mixture of potential carcinogens and mutagens (see Tables 9 and 13), was relatively low compared to studies for finished drinking water supplies. The most likely explanation is that the chlor-alkali wastewater extracts were only concentrated 250 fold, whereas the drinking water extracts in the studies referred to above were concentrated up to 200,000 fold. The toxicological tests noted in Table 13 used relatively high doses, which may or may not reflect a low-level response for these chemicals.

Other reasons might be the recognized uncertainties regarding the efficacy of various in vitro assay methods for detecting mutagenic substances in wastewaters. Some possible reasons are:

a) The mutagenic agents are so diluted in the wastewaters that negative results are obtained. This does not necessarily indicate, however, the absence of mutagens.
b) There is a potential for obtaining false positives as well as false negatives.
c) Mutagens may be preferentially lost during sample preparation.
d) Some compounds may have been chemically altered during concentration extraction or storage.
e) The complexity of the mixtures may lead to a variety of additive and antagonistic effects. Some fractions may be too toxic for reliable determinations of mutagenicity.

It has been shown in some studies that the specific activities of basic and possibly neutral fractions tested are considerably higher than those of the total extracts. Any future studies should consider testing extracts that have been separated into acid, base, and neutral fractions as well as using the standard plate technique for straight effluent samples.

In summary, the genotoxicity test data from the very limited number of samples of chlor-alkali effluent are inadequate for the assessment of possible human health hazards and other environmental impacts. These tests, however, should contribute to the setting of priorities in ranking pollution problems.

2.6 Pollution Abatement Options and Treatment Technology

2.6.1 Conventional Pollutants. In-plant process modifications can significantly reduce pollutant loads discharged from chlor-alkali plants. In 1970-71 many modifications reduced conventional pollutant loadings as well as priority pollutant discharges. The modifications were in the form of segregation of contaminated wastewaters from relatively clean wastewaters, recycling of as much contaminated wastewater as practical, and the treatment of the remaining contaminated wastewaters. Other in-plant modifications, which help to reduce pollutant discharges, include the following:

Anode Material

All plants now use metal anodes rather than graphite anodes. The use of dimensionally stable anodes (DSA) increases current efficiency, greatly reduces the pollutant load of priority organics present in plant wastewaters, and produces higher purity cell gas, which reduces the amount of gas necessarily vented from the chlorine liquefaction system. (Also, the use of refrigeration equipment for chlorine recovery reduces the amount of chlorine gas vented from the chlorine liquefaction system even more).

Tail Gas Emisson Control

The amount of chlorine present in the tail gas is important, as this gas has to be removed and treated or used before being vented to the atmosphere. At all plants the chlorine gas is scrubbed with caustic soda to produce sodium hypochlorite. The hypochlorite is sold by some plants; however, at other plants this waste stream is treated or partially treated before being discharged.

Catalytic decomposition involving the use of small amounts of nickel or iron salts, followed by a retention for two or three days is the most common treatment method used; however, a residual of a few parts per million chlorine are still normally present in the effluent discharged. The complete removal of residual chlorine is only practiced at one plant using hydrogen peroxide. Alternatively, dechlorination can be accomplished by the addition of sulphur dioxide, sodium bisulphite, or sodium metabisulphite.

Chlorine Condensates and Spent Drying Acid

Other sources of chlorine releases in discharged wa. ewaters are chlorine condensates and spent drying acid. Stripping techniques, such as steam or vacuum stripping, may be applied to recover the chlorine, which is frequently returned to the

process for purification and recovery. A few milligrams of residual chlorine per litre of effluent are sometimes discharged with the final effluent.

Besides the in-plant control practices, further treatment is usually required for the wastewater streams. In general, these streams may be divided into cooling water and process wastewater.

Once-through cooling water should be relatively free of suspended solids and dissolved salts, except when seawater is used. Any contaminants present (when fresh-water is used for cooling) would come from leaks which should be detectable using monitoring equipment. In any event, contaminants present in cooling water should be very low, and treatment should not normally be required.

Process wastewaters, on the other hand, do require treatment. Suspended and dissolved solids, and residual chlorine are the major conventional pollutants that could be of concern in the production of caustic chlorine by the mercury cell process.

Brine purification muds constitute the major source of suspended solid wastes generated at these plants. These solids are removed from all plant wastewaters by filtration or settling. In addition, mercury-contaminated wastewaters that have been treated for mercury removal are filtered or decanted to prevent solids from becoming part of the final effluent. The only suspended solids discharged originate from non-mercury- contaminated areas (the cleaning of equipment or washdown) and surface runoff. The foremost industrial treatment for removing suspended solids is a 24-hour retention pond. Only Plant No. 3 has a pond for treating the combined plant effluent. The average concentration of suspended solids in the final effluent from this plant is 2 mg/L.

Most of the chlor-alkali wastewaters are either acidic or alkaline, or react with water to give acidic or alkaline solutions. Before disposal in surface waters the pH has to be monitored: excess acidity or excess alkalinity need to be adjusted to normal and controlled. Control of excess acidity or alkalinity is best accomplished by taking advantage of available acid waste streams to neutralize basic waste streams, and vice versa. If no hold-up facilities are available, wide excursions in pH can occur as noted for most plants.

As mentioned above, hypochlorite solutions are used, sold, or decomposed; chlorine condensates and spent drying acid are normally steam- or vacuum-stripped to remove chlorine. However, residual chlorine concentrations normally low but high during occasional plant upsets are sometimes present in the effluent from the plant. These discharges are of concern because chlorine in very low concentrations is toxic to fish, and

the interaction between residual chlorine and organic compounds may lead to the formation of chlorinated hydrocarbons.

Dechlorination may be carried out by reacting chlorinated solutions with any of a number of chemicals; however, SO_2 appears to be the most economical and accepted method. The reaction is almost instantaneous and should be satisfactory for in-line applications where the concentraton of residual chlorine is fairly constant. Where high peaks of concentration occur, a hold-up system is required to equalize the concentration. At Plant No. 3 (with the 24-hour retention pond) 100 percent of the chlorine is normally removed using hydrogen peroxide.

2.6.2 Priority Pollutants. Mercury is the major priority pollutant of concern in the production of chlorine by the mercury cell process. Other toxic metals found in fairly minor concentrations in the final effluent are shown in Table 9. Sources of these metals are the intake water, salt impurities, and possibly corrosion products from the reaction between chlorine and process equipment.

Brine mud wastes that contain low concentrations of mercury, after the muds have been filtered or dredged from holding ponds, are disposed of at authorized landfill sites or buried in well constructed burial pits. Other solids containing high mercury concentrations are leached with hypochlorite, retorted, or stored for mercury recovery.

All leaks and spills are collected and recycled or added to the mercury-contaminated wastewaters that are then sulphide-treated to remove mercury before being discharged. The sulphide treatment of wastewaters to remove mercury has the additional benefit of removing other metals at the same time.

A summary of abatement options and methods to treat mercury-bearing streams are shown in Table 14.

Methods to control mercury releases into the air are not covered in this report; however, refrigeration of hydrogen gas and cell vent gases, for example, followed by their passage through carbon beds or molecular sieves reduces the mercury emissions and reduce atmospheric fallout in the neighbourhood of the plant and in turn should reduce mercury concentrations in storm runoff. At most plants relatively clean runoff is diverted away from the plant. Collected runoff is checked for mercury content; if it is high, the runoff is treated for mercury removal.

Priority organic pollutants were also found in measurable concentrations in the final effluent. Table 15 lists these compounds and their concentrations; it also shows the aquatic fate of these contaminants and best practical treatment methods to remove these contaminants from wastewaters.

TABLE 14 WASTE STREAMS FROM MERCURY CELL PLANTS WITH ABATEMENT OPTIONS AND TREATMENT

Source and Comments	Components	Abatement Options	Treatment
Waste sludges from saturators and brine purification	$CaCO_3$ $CaSO_4$ $Mg(OH)_2$ Heavy metal hydroxides Mercury	The solids are filtered	Since the solids contain small amounts of mercury, they should go to a secure landfill site.
			The filtrate is recycled to brine circuit or sulphide-treated for Hg removal before being discharged. The filter wash water is recycled or sulphide-treated for mercury removal.
		Sent to a lagoon	The solids settle in the lagoon. The wastewater is recycled to the plant or sulphide-treated for Hg removal before being discharged. Any seepages are collected and treated for mercury removal.
		Mercury is leached	The solids are treated with sodium hypochlorite to recover mercury as the chloride. The solids can then be safely disposed of to landfill. The mercury-chloride-containing solution is recycled to brine makeup.
		Sent to salt cavity	None of the remaining mercury cell plants use solution mining.
Cell room wastewaters containing leaks, spills purged brine, housekeeping wastewaters, end box cooling purge, etc.	Salt, caustic, hypo, misc. dirt, mercury, sulphates	Recycle/reuse as much as possible Sulphide treatment for mercury removal	Destroy any hypo present, adjust pH to 6-8, sulphide-treat for Hg removal, filter, and discharge to sewer. Treated effluent contains about 40 ppb Hg. Solids retorted for Hg recovery.
			Some plants use ponds to sulphide-treat the mercury-contaminated effluents. The solids settle, and the supernatant is syphoned to sewer.
			An activated-carbon column is sometimes used after filtration. This treatment should further reduce the Hg concentration.
Spent sulphuric acid from chlorine drying towers	H_2SO_4	Can be regenerated Used for pH control of wastewaters Shipped off-site for reuse (e.g. fertilizer production)	Normal practice is to ship the acid off-site or dechlorinate the acid in a stripper and discharge to sewer after neutralization.
Tail gas scrubber solution	NaOCl or $Ca(OCl)_2$	Sell Use in pulp and paper mill Use for extraction of Hg from muds Decompose	If the hypochlorite cannot be sold or used, it is normally decomposed and recycled to the brine circuit or discharged to sewer.
Caustic filter backwash	NaCl, Mercury, filter aid, NaOH	Send to holding tank	Supernatant can be filtered or decanted and used for pH control of brine.
			Solids can be retorted or leached with hypo for mercury recovery.
			Filtrate or decanted wastewaters can be added to cell room wastewaters for Hg removal before discharging to sewer.
Hydrogen and vent gas condensates	Mercury vapor Water vapor	Recycle	Gases cooled in primary coolers - condensate and mercury returned to denuder. Hydrogen then refrigerated to condense and recycle mercury. Condensate recycled to process or cooling tower.
		Treat	The condensate is added to the cell room wastewater for sulphide removal of mercury.

Individual waste streams were not monitored for priority pollutants, thus the point of origin of these pollutants within the plant was not established. Treatment methods used to remove chlorinated organics from the entire plant effluent would be far too costly for the benefits obtained, as the significance of low concentrations of priority pollutants found has not yet been established. Individual streams could be monitored for chlorinated hydrocarbons to determine which streams contain the bulk of the priority contaminants. Some effort could then be made to remove them by using one of the treatment methods noted in Table 15.

2.6.3 Selection of Appropriate Technology. At present the following technology is recommended to treat liquid effluents from mercury cell chlor-alkali plants:

1) Brine saturator and treatment solids should be filtered from the brine, washed to remove residual brine containing soluble mercury, and disposed of at an authorized landfill site. The filtrate and wash water should be recycled to the brine circuit.
2) Any brine saturator and treatment solids, which contain over 50 mg/kg of mercury, should be treated for mercury removal before being disposed of at an authorized landfill site.
3) Contaminated wastewaters should be segregated from clean wastewaters (containing only minor concentrations of mercury) and recycled or reused if possible. The remainder of the mercury-bearing wastewater should first be sulphide-treated to remove mercury and then filtered under pressure. The treatment solids should be treated for mercury recovery and the filtrate should join other wastewaters from the plant.
4) All caustic should be filtered to remove mercury and other minor impurities. Solids from the filter backwash should be treated for mercury recovery. The wash water should be reused.
5) The combined wastewaters; i.e., process waters, cooling water, and storm runoff, should go to a retention system where any solids present would settle. The pH should be controlled, and the effluent dechlorinated using such an established procedure as the addition of peroxide or sulphur dioxide.

TABLE 15 THE AQUATIC FATE AND POSSIBLE TREATMENT METHODS FOR PRIORITY POLLUTANTS FOUND IN FINAL EFFLUENT FROM MERCURY CELL CHLOR-ALKALI PLANTS

PARAMETER	LEVELS FOUND IN C-A EFFLUENT (ug/L)	AQUATIC FATE[1]					
		Photolysis	Hydrolysis	Volatilization	Sorption	Bioaccumulation	Treatment[2]
Chloroform	T-410	Probably not significant	Probably not significant	Primary transport process	Probably not significant	Weak to moderate	Steam stripping and activated carbon adsorption considered best
Carbon Tetrachloride	T-24	Probably not significant	Too slow to be significant process	Primary transport process	No clear evidence of selective conc'n in sediments	Inconclusive	Gas flotation, GAC adsorption and sedimentation with alum and lime addition
1,2-Dichloroethane	T-12	Appears to be insignificant	Probably too slow to be significant	Primary transport process	Probably not important	Probably not significant	Sedimentation with alum and polymer addition
Trichloroethylene	T-72	Probably does not occur	Probably too slow to be significant	Primary transport process	Probably not important	Evidence of some accumulation by marine organisms	Gas flotation, activated sludge. GAC adsorption and reverse osmosis
Bromodichloromethane	T-28	No information found	Too slow to be significant fate	No specific info. Probably serves as significant transport	No specific info.	May bioaccumulate	Gas flotation with alum and polymer addition or GAC adsorption
2,4,6-Trichlorophenol	T-6	Been reported but relevance uncertain	Not thought to be relevant	Probably not significant	Definite potential for sorption by organic material likely	Probably not important	Aerated lagoons and powdered activated carbon adsorption
2-Nitrophenol	T-1	Slow photolysis may be main degradative path	Slight possibility if sorbed by clay	Probably not important	Adsorption by clay demonstrated	Probably not important	Sedimentation, activated sludge and powdered activated carbon adsorption
4-Chloro-m-cresol	T-3	Intramolecular photolysis most probable fate	Not relevant process	Probably not significant	Insufficient data. Probably not important	Probably not significant	Activated sludge and GAC adsorption
Toluene	T-2	Direct photolytic cleavage is energetically improbable	Not significant	Significant process	Cannot be determined	Probably not important	Biological degradation, GAC adsorption and steam stripping or aeration
1,1-Dichloroethene	T-19	Negligible	Probably occurs too slowly to be significant	Appears to be primary transport process	Little information probably insignificant	Little information likely insignificant	Filtration, sedimentation with alum and polymer addditions and PAC adsorption
1,1,1-Trichloroethane	T-94	Probably not significant	Probably occurs too slowly to be significant	Primary transport process	Probably not important	Probably not important	Activated sludge (likely due to stripping) and carbon adsorption

TABLE 15 THE AQUATIC FATE AND POSSIBLE TREATMENT METHODS FOR PRIORITY POLLUTANTS FOUND IN FINAL EFFLUENT FROM MERCURY CELL CHLOR-ALKALI PLANTS (Cont'd)

PARAMETER	LEVELS FOUND IN C-A EFFLUENT (ug/L)	AQUATIC FATE[1]					
		Photolysis	Hydrolysis	Volatilization	Sorption	Bioaccumulation	Treatment[2]
1,2-Dichloropropane	T	No data	No data, probably important	Compound volatile but may return through precipitation	No data, may be adsorbed moderately	No data, may bioaccumulate slightly	Activated sludge and GAC adsorption
Trans-1,3-Dichloropropene and cis	T-4	No data	Appears to be slow, but may be important	Primary transport process	No data	No data, probably not important	Biodegradation
1,1,2-Trichloroethane	T-14	Probably not significant	Probably occurs too slowly to be significant	Probably primary process	Inconclusive	Inconclusive	Activated sludge (likely due to stripping) and carbon adsorption
Dichloromethane	T-55	Probably not significant	Probably not a significant fate	Primary transport process	Probably not significant	Probably does not significantly bioaccumulate	Sedimentation with alum addition or gas flotation with alum addition
1,1-Dichloroethane	T	Probably not significant	Probably occurs too slowly to be significant	Primary transport process	Probably not important	Probably does not significantly bioaccumulate	Sedimentation, activated sludge
Trans-1,2-Dichloroethylene	0-23	Probably does not occur	Probably occurs too slowly to be significant	Appears to be primary transport process	Probably insignificant	Probably insignificant	Gravity oil separation
Ethylbenzene	T-1	Direct photolytic cleavage is energetically improbable	Not significant	Significant transport process	Relative importance cannot be determined	Probably not important	Gas flotation, filtration or aerated lagoons
1,4-Dichlorobenzene	0-9	No information	Probably will not hydrolyze in water	Probably volatilizes from water at rapid rate	May be substantial	Will likely bioaccumulate in the lipids of tissue of living organisms	Aerated lagoons or activated sludge
Diethylphthalate	T-3	Probably does not undergo direct photolysis	Not considered a competitive process	Not as important as adsorption	Sorption onto S.S. and biota probably most important	Considered an important fate process	Sedimentation with chemical addition and activated sludge
Di-n-Butylphthalate	T-16	Probably does not undergo direct photolysis	Not considered a competitive process	Not as important as adsorption	Sorption onto S.S. and biota probably most important	An important fate process	Gas flotation with chemical adddition, sedimentation with chemical addition and GAC

TABLE 15 THE AQUATIC FATE AND POSSIBLE TREATMENT METHODS FOR PRIORITY POLLUTANTS FOUND IN FINAL EFFLUENT FROM MERCURY CELL CHLOR-ALKALI PLANTS (Cont'd)

PARAMETER	LEVELS FOUND IN C-A EFFLUENT (ug/L)	AQUATIC FATE[1]					
		Photolysis	Hydrolysis	Volatilization	Sorption	Bioaccumulation	Treatment[2]
Bis(2 ethylhexyl)phthalate	T-4	Probably does not undergo direct photolysis	Will hydrolyze slowly not a competitive process	Not as important as adsorption	Probably most important transport process	An important fate process	Sedimentation with chemical addition, aerated lagoons and powdered activated carbon
Phenol	0-1	May be an important degradative process in aerated clear waters.	Not significant	Possibility of some phenol passing into atmosphere	Not significant	Not significant	Sedimentation with alum addition, aerated lagoons, GAC adsorption or R.O.

1. From EPA "Water-Related Environmental Fate of 129 Priority Pollutants".
2. From EPA "Treatability Manual" Volume 1.
T = Trace

3 DIAPHRAGM CELL PROCESS

3.1 Process Description

In the diaphragm cell a layer of asbestos is used to separate the anode from the cathode. This asbestos layer allows ions to pass through by electrical migration but reduces diffusion of products. Diaphragms permit the construction of compact cells of lowered resistance because the electrodes can be placed close together. Because of their resistance, these cells require a higher voltage and a higher hydrostatic pressure on the brine feed. (See Figure 3 for a schematic of the diaphragm cell.) Purified, saturated brine, which flows to the cells, is electrolyzed to produce chlorine, caustic soda, and hydrogen as shown by the equation:

$$2NaCl + 2H_20 \rightarrow Cl_2 + 2NaOH + H_2$$

Chlorine is formed at the graphite or dimensionally stable anodes, bubbles to the top of the cell, and removed in the chlorine header. The cathode is a steel wire mesh coated with an asbestos layer. The sodium ions migrate to the cathode. At the cathode, hydroxyl ions and hydrogen are formed. A solution containing 10 to 15 percent NaOH is generated in the cathode compartment.

The diaphragm hinders back-migration of hydroxyl ions to the anode area, where they would react with the chlorine to form chlorates and also reduce current efficiency.

The hydrogen is piped from the cells, cooled to remove water, and then burned for fuel or used as a chemical synthesis material.

The brine liquor withdrawn from the cathode contains the sodium hydroxide formed there as well as 12 to 15 percent NaCl, because only about 50 percent of the salt is decomposed at optimum cell operating conditions. This liquor is concentrated in multiple-effect evaporators to produce a 50-percent caustic soda product containing about one percent salt. Salt, which crystallizes out during the concentration step is removed by filtration or centrifugation, and recycled to the brine circuit.

A schematic flow diagram of the diaphragm cell plant is shown in Figure 4.

If further purification is required, the caustic can be purified by any one of several proven techniques. The most common is an anhydrous ammonia extraction process, which removes chlorates and a number of other minor inorganic salt impurities, including the sodium chloride.

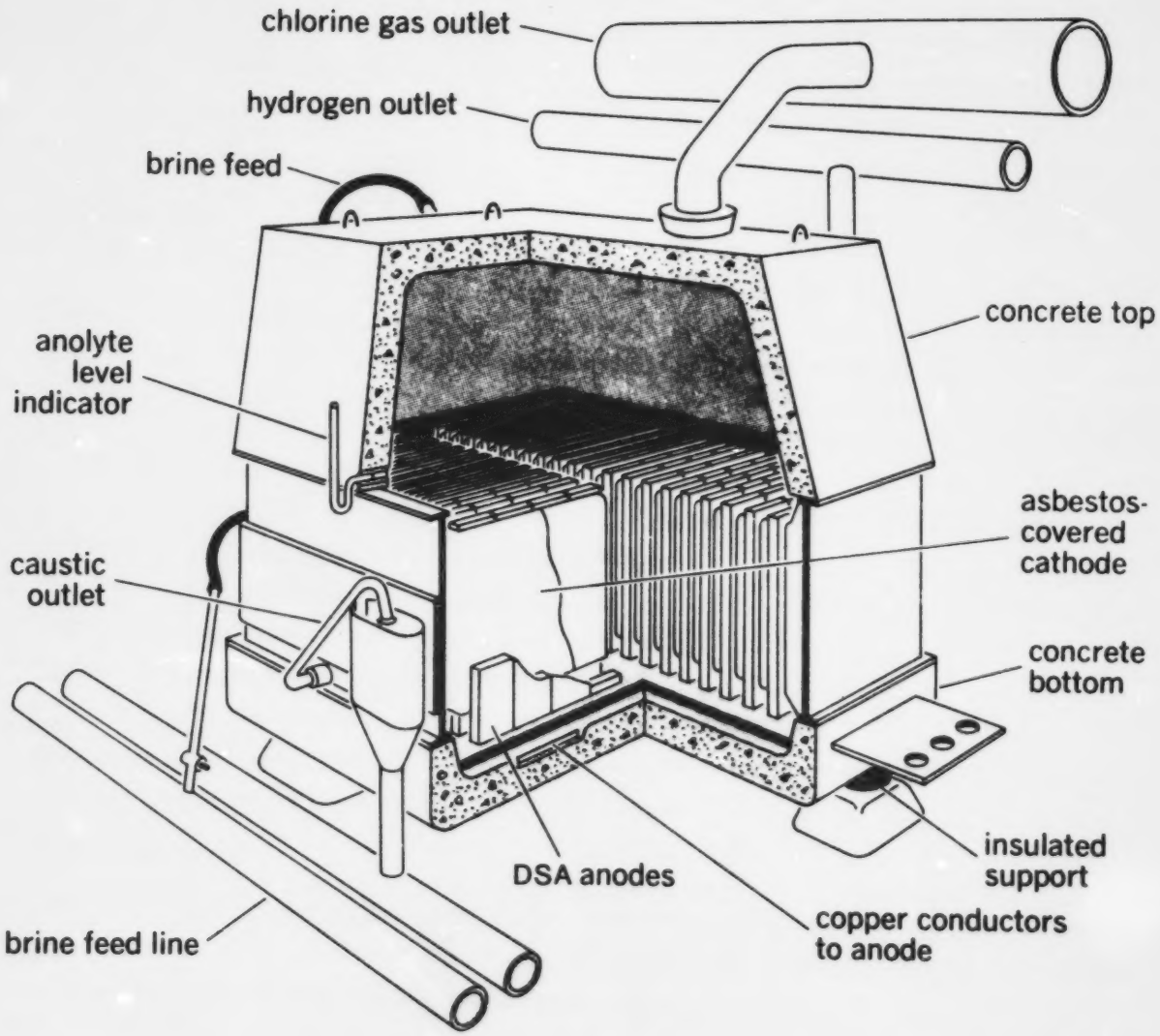


FIGURE 3 SCHEMATIC DIAGRAM OF HOOKER TYPE S-3C DIAPHRAGM CELL

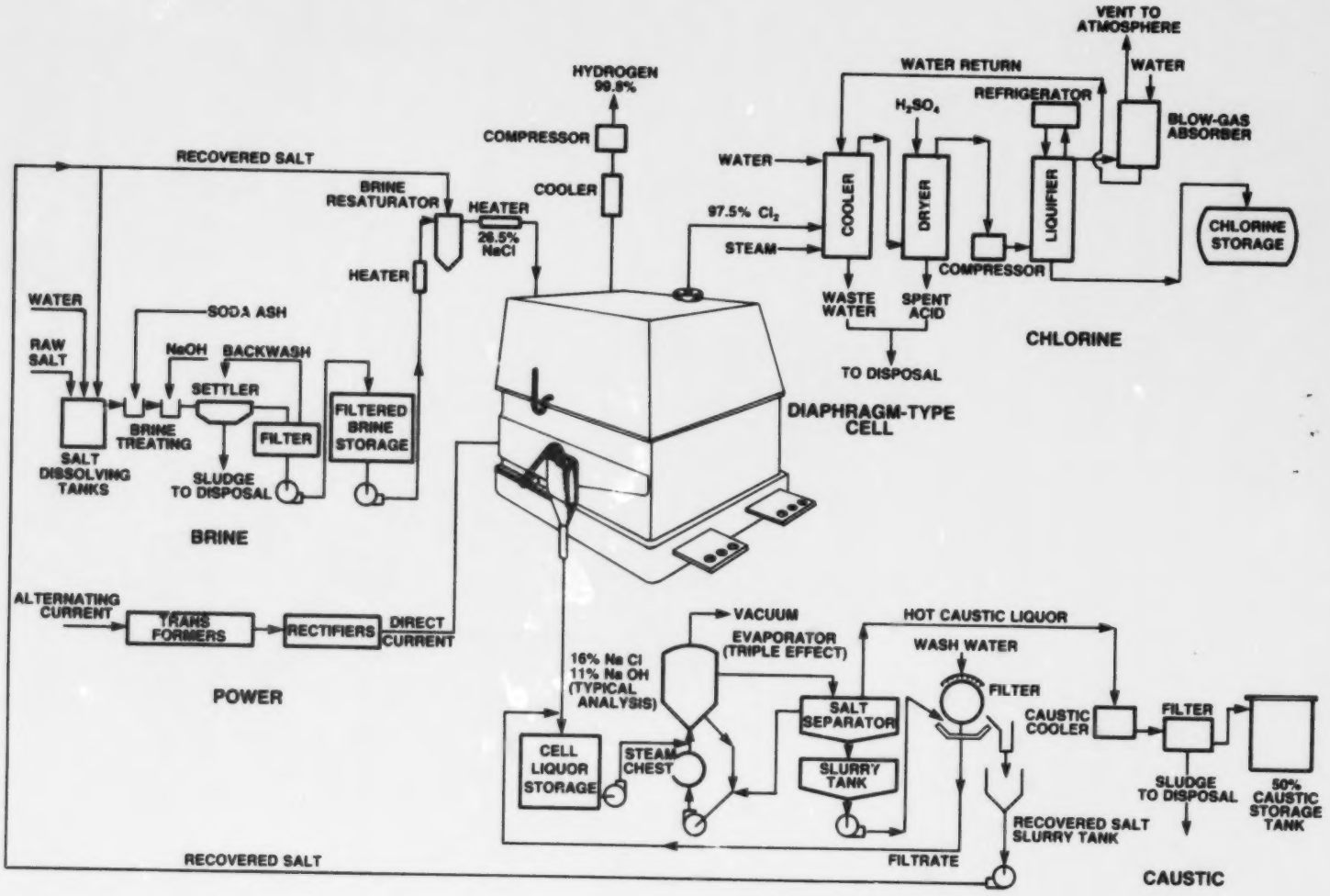


FIGURE 4 FLOW DIAGRAM OF A TYPICAL DIAPHRAGM-CELL CHLOR-ALKALI INSTALLATION (Taken from EPA Report No. AP80 "Atmospheric Emissions from Chlor-Alkali: Manufacture")

3.2 Water Use and Wastewater Sources

3.2.1 Water Use. Common uses of water in diaphragm cell plants can include non-contact cooling, tail gas scrubbing, cell washing, general housekeeping, brine make-up, filter backwashing, and water used for the evaporation of the caustic.

The total water usage at diaphram cell plants was found to range from 14 cubic meters per tonne of chlorine produced, (when cooling towers are used), to 475 cubic meters per tonne of chlorine produced (for once-through cooling systems). Non-contact cooling water comprises approximately 0 to 97 percent of the total water usage. (The use of water for non-contact cooling is not covered by this report.)

3.2.2 Wastewater Sources

Dissolver Slurry

As discussed in Section 2.2.2, about 30 to 100 kg of waste solids (mainly anhydrite and gangue) are produced per tonne of chlorine produced, if rock salt is used as the raw material. This solid waste is either pumped to settling ponds or discharged to the ocean. If settling ponds are used, the weak brine is recovered and recycled.

Brine Mud

The amount and type of solids discharged are similar to those discussed under mercury cell plants, except that there should be no mercury in the solids or the slurry. The brine muds are filtered and used for on-site landfill, or discharged into the ocean, sent to settling ponds, salt cavities, or deep wells. If ponds are used, the mud is periodically removed and used for landfill.

The amount of clarifier slurry discharged ranges from 0.08 to 0.3 cubic meters per tonne of chlorine produced with a content of solids ranging from 5 to 20 percent. The brine and wash waters are normally recycled.

Cell Room Wastes

The major components of cell room wastes includes leaks, spills (brine, caustic soda, hypo, etc.), asbestos slurry (used asbestos diaphragm material hosed off the cathode section) and general housekeeping wastewaters.

The amount of wastewaters varies from plant to plant and depends on operating practices. For instance, the asbestos slurry is intermittent, yet averages about 0.07 cubic meters per tonne of chlorine produced.

If graphite anodes are used in cells, the wastewater could contain higher chlorinated organics levels.

Chlorine Cooling Condensate

Condensate from the indirect cooling of chlorine gas is reused in other plants on the integrated plant site or stripped of chlorine by steam injection in a packed tower; then recyled to the process.

At some plants the hot, wet chlorine gas is cooled by direct contact with sea-water. After the sea-water has been stripped of its chlorine, it is discharged into the sewer. No condensate flow values are available.

Spent Sulphuric Acid

After the chlorine gas has cooled, it is dried in a series of sulphuric acid drying towers. The spent acid (50 to 70% H_2SO_4) is collected and reused, regenerated, sold, used for pH control, or discharged directly to the sewer.

Tail Gas Scrubber Liquid

The residual uncondensed chlorine gas from the liquefaction step is either used to produce sodium hypochlorite or burned with hydrogen to produce muriatic acid. The waste gas hypochlorite absorption units are also used to absorb (a) gases on start-up and in emergency situations, (b) waste gas from returned tank cars, cylinders, etc.

This hypochlorite can be used in other processes, sold, decomposed, or discharged to the sewer. No flow figures are available.

Filter Backwashers

A sodium sulphate purge, made by backwashing the precipitated salt slurry on the filter during the concentration of sodium hydroxide by evaporation, ensures satisfactory diaphragm cell operation. This sulphate purge is discharged to the sewer, returned to the brine purification step where it is removed by precipitation, or recovered for sale.

Brine filter backwash is either discharged to a brine settling pond, brine wells, or collected in a holding tank. At plants using holding tanks, the supernatant is recycled to the process and the concentrated solids discharged to the ocean.

The backwash from the raw-water filter is either sent to a treatment pond or brine-settling pond, or discharged into the sewer.

The caustic produced is filtered to remove impurities. The filter backwash is recycled to the process.

Hydrogen Condensate

Cooling of hydrogen gas for use or sale produces a condensate which is discharged directly to the sewer or reused.

Barometric Condenser Wastewater

The barometric condenser, used to evaporate caustic, collapses the hot vapours from the evaporator, thus creating a high vacuum in the system. Large amounts of water are required for this. Based on the results from two plants, the barometric condenser flow averages 77 m3/kkg of chlorine produced in once-through systems. This wastewater contains about 10 mg/L of caustic carry-over plus a small amount of salt and sulphate.

Boiler Blowdown

Another waste stream which ends up in the wastewater collection system is boiler blowdown. The approximate composition (in mg/L) of this wastewater is as follows:

dissolved solids	2000 - 3000
suspended solids	10
chlorides	100 - 200
sulphates	75 - 100
silicia	3 - 5
iron	50 - 10
phosphates	0 - 25
chelates	15 - 25.

At some plants this blowdown is recovered and pumped to the dissolvers.

Cooling Tower Blowdown

About one third of the diaphragm cell chlor-alkali plants use cooling towers. Generally, the blowdown enters the main effluent stream without treatment. The composition (in mg/L) of the blowdown stream is approximately as follows:

dissolved solids	400 to 700
chlorides	200 to 300
sulphate	100 to 200

calcium	100 to 150
chromate	12 to 15
and zinc	0 to 2

Sanitary Effluents

Sanitary effluents from these plants go to anaerobic/aerobic ponds, municipal treatment systems, septic tanks, or directly into the combined effluent without treatment.

Storm Runoff

The quantity and quality of storm runoff is site-specific and depends on the precipitation rate and general yard maintenance.

At most plants the storm runoff is not treated for the removal of solids or pH adjustment. The flow is directed to the final discharge stream.

Summary of Wastewater Flows

Wastewater flows, which includes process wastewater, cooling tower blowdown, wastes from water treatment facilities, boiler blowdown (if not reused), and runoff from land used for the disposition of wastewater and sludges associated with the operation of a plant averages 5,500 liters per tonne of chlorine produced (Table 16) for the six diaphragm cell plants where data has been gathered. For new plants a wastewater flow of less than 2000 liters/kkg of chlorine produced could be attained.

TABLE 16 SUMMARY OF WASTEWATER FLOW DATA FROM CHLORINE DIAPHRAGM CELL PLANTS

	WASTEWATER FLOWS (m^3/tonne)		
Plant No.	Process	Once-Through Cooling	Total
1	7.9	191.0	198.9
2	6.2	94.5	100.7
3	9.0	--	9.0
4	9.6	115.0	124.9
5	0.4	360.0	360.4
6	0	--	0
Ave. for 6 plants	5.5		

In the United States, diaphragm cell plants using dimensionally stable anodes and recirculated barometric water use an average of 2400 L/kkg chlorine produced.

3.3 Conventional Pollutants - Methodology for Data Collection

3.3.1 Methodology. The collection of data on conventional pollutant concentrations and flows of process wastewater streams was compiled using a three-way data-gathering system. In 1973, a questionnaire was distributed to diaphragm cell plants requesting detailed information on flows, and pollutant concentrations present in process and cooling waters.

Subsequent to that time, a number of surveys by EPS Regional personnel and by their Provincial counterparts have been carried out over the past 8 years. In addition, some plants are required to submit data monitored monthly to their respective Provincial Ministry for the Environment.

This data appears in Sections 3.4 for the six diaphragm cell plants operating in Canada.

3.3.2 Description of Specific Plants. The following discussions primarily covers plant practices in water pollution control and treatment of wastewaters generated in diaphragm cell chlor-alkali plants in Canada.

Plant No. 1

At Plant No. 1, solar-evaporated salt is dissolved in fresh and recycled water. The raw brine, which contains impurities such as calcium, magnesium, and other minor impurities is purified by raising the pH of the brine to between 10 and 11 with sodium hydroxide or sodium carbonate, or both. (The sodium carbonate is produced at the plant by treating cell liquor with power house flue gas, and dilute caustic soda.) Heavy metals and magnesium are precipitated as hydroxides and calcium as the carbonate.

The precipitated material is allowed to accumulate in the treatment tanks for two or three months. The heavy sludge is then hosed out to a sludge holding tank. The supernatant brine is filtered, heated, resaturated with salt recovered in the evaporation of caustic cell liquor, and then sent to the diaphram cells. Backwash from the brine filters is sent to the sludge holding tank. The combined slurry (brine treatment solids plus filter backwash) is released to the sewer at a controlled rate.

Cell room losses, which consist of leaks, drips, spills, wash-down waters, etc. are normally small. These drainings are collected in a sump and pumped back to the brine circuit for recycling. Wastewaters from the cell renewal area, which contains a high

concentration of asbestos fibres, are sent to a settling pond. Most of the wastewater seeps into the ground. Periodically, the asbestos fibre is removed and buried at a landfill site.

The hot, wet chlorine gas from the cells is cooled by direct contact with sea water, dried by passing the gas through three towers filled with progressively stronger sulphuric acid, further cooled by direct contact with liquid chlorine, purified, and liquefied. The spent sulphuric acid, at a strength of about 70 percent, is sent to the chlorine stripper. (Chlorine in the seawater used for direct chlorine-cooling is stripped down to a residual concentration of less than 5 mg/L). This water, containing the purged sulphuric acid, is then discharged to the sewer.

The uncondensed chlorine gas from the liquefaction stage is either sent to muriatic-processing or scrubbed with sodium hydroxide to produce sodium hypochlorite. Vent gases from empty rail cars, storage tanks, and barge tanks are also sent to the hypo-absorption system. This hypochlorite is decomposed and recycled to the brine circuit.

Hot hydrogen gas from the cells is cooled, compressed and used as fuel in the boiler or mixed with chlorine and burned to produce 35 percent muriatic acid. During the manufacture of HCl, the unabsorbed hydrochloric acid gas is passed through a tail gas scrubber for additional absorption. The tails scrubber vent gas passes into a sea-water ejector separator to remove all traces of hydrochloric acid. This waste stream goes to the sewer.

The cell liquor, which contains about 14 percent caustic soda plus about 13 percent salt is sent to triple-effect evaporators to concentrate the sodium hydroxide to 50 percent. In this process, salt which crystallizes out of solution, is recovered by filtration, washed relatively free of caustic, and recycled to the brine resaturator. The first-stage wash water is returned to the evaporator. The second-stage wash water is sent to the brine circuit. The caustic is cooled, centrifuged to remove more salt and sodium sulphate, and then stored. The slurry of solids from the centrifuge is recycled to the brine area. When vapours from caustic evaporators are contact-cooled using barometric condensers, a significant amount of wastewater can be generated. At this plant about 90 m^3 of sea-water per tonne of chlorine produced, containing a small amount of caustic soda, is discharged directly to the sewer. Some of the 50-percent caustic soda is further concentrated to 73 percent for some customers.

Boiler blowdown, which contains some phosphates, sulphite, caustic soda, silica, and sodium chloride is discharged to the sewer.

Because of the porosity of the soil around the plant, most of the rainwater seeps into the ground, thus there is little runoff.

Total waste water from this plant is monitored daily; the data are presented in Table 17. As noted in this table, the addition of metallics to the wastewaters is insignificant (the amount of metallics added from the plant; final effluent volume times concentration minus intake water volume times concentration). Of concern can be the occasional addition of residual chlorine and suspended solids, and some wide excursions in pH. Neither the discharges of metallics nor those of conventional pollutants should be of concern.

Plant No. 2

At Plant No. 2 the operating process and procedures are fairly similar to those noted for Plant No. 1 since both plants are owned by the same company. For example, in both plants solar salt is used; both plants use dimensionally stable anodes; the same type of cell is used; the hot, wet chlorine gas is cooled by direct contact with sea water; triple-effect evaporators with barometric condensers are used; and about 95 percent of the water used in the plant is sea water for cooling purposes. Plant No. 2, however, is smaller and some unit processes as noted below are not carried out, thus the quality and quantity of wastewaters discharged are somewhat different (Tables 17 and 18). The major operating differences at Plant No. 2 are:

i) Chlorine gas is piped to a pulp mill after cooling, drying, purification, and compression. (There is no liquefaction equipment.)
ii) No hydrochloric acid is produced,
iii) No 73 percent NaOH is produced,
iv) The cell room floor drainings are discharged to the sewer.

The first three differences noted above are not likely to affect the quality of the wastewaters, only the quantity. The cell room drainings could result in higher levels of asbestos being discharged; however this analysis was not undertaken on Plant No. 2 effluent. Very few analyses for metallics have been performed, thus no conclusions can be made, but it would appear as though the additions of metallics to the wastewaters from this plant could be insignificient. The three conventional parameters that might be of concern at times are pH, residual chlorine, and suspended solids.

TABLE 17 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 1 DIAPHRAGM CELL CHLOR-ALKALI PLANT

Parameter	Intake Water (mg/L)	FINAL EFFLUENT			
		No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow (m^3/d)**			82000		
pH**	7.1	1430	7.5	2.3-12.4	
Total Solids		8	26840*		
Suspended Solids	<5	1385	19	0-1074	4.0
Spec. Cond. umhos/cm			24	32850*	
Residual Chlorine		1400	0.4	0-49	0.085
TOC	10	2	10		
BOD_5	4	2	<2		
Hardness		1	4310		
Sulphate	2065	2	2000*		
Chloride	15000	9	13250*	11000-14200	
Total Barium	0.0006	7	1.01		0.21
Dissolved Ba		2	0.5		0.10
Total Cadmium	<0.001	2	<0.001		
Total Cobalt	<0.002	2	<0.002		
Total Chromium	<0.002	2	<0.002		
Total Copper	<0.001	79	0.095	0.005-4.1	0.020
Dissolved Cu		2	0.03		
Total Manganese	0.0037	2	0.0014		0.0003
Total Molybdenum	<0.02	2	<0.02		
Total Nickel	<0.008	2	0.01		0.002
Dissolved Ni		2	0.01		0.002
Total Lead	<0.008	2	<0.008		
Total Antimony	<0.008	2	<0.008		
Total Tin	<0.02	2	<0.02		
Total Titanium	<0.0009	2	<0.0009		
Total Iron	0.057	80	0.26	0.02-1.8	0.042
Dissolved Fe		2	0.16		0.038
Dissolved Ca		2	260*		
Dissolved Mg		2	888*		
Dissolved K		2	270*		
Dissolved Na		2	7500*		
Total Zinc	0.050	78	0.06	0.001-1.7	0.002
Dissolved Zn		2	0.06		0.014
Total Mercury	<0.0002	2	<0.0002		

Note: This plant was monitored in the toxic chemical screening study.

* These high values are due to the fact that about 95 percent of the wastewater discharged is seawater.

** Units in the column headings do not apply here.

TABLE 18 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 2, DIAPHRAGM CELL CHLOR-ALKALI PLANT

	FINAL EFFLUENT			
Parameters	No. of (Values)	Ave. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow (m^3/d)**		11800		
pH**	1683	7.8	2.0-12.8	
Total Solids	1	34450*		
Suspended Solids	83	12.5	0-74	1.48
Spec. Cond.	9	42478*	37600-44700	
Chloride	2	15212*		
Residual Chlorine	1824	0.06	0-3.5	0.007
Total Copper	1	0.04		0.0047
Total Iron	1	0.41		0.048
Total Nickel	1	0.01		0.0012
Dissolved Sodium	1	8550*		
Dissolved Oxygen	4	8.3	7.7-9.1	
Total Alkali	1	62		
COD	1	20		2.4

* These high values are due to the fact that about 95 percent of the wastewater discharged is seawater.
** Units in column heading do not apply here.

Plant No. 3

At Plant No. 3, rock salt is dissolved in both fresh and recycled water; i.e., water recycled from the brine sedimentation pond, chlorine condensate, wash water from the cell room, and some cooling water. The raw brine, which contains impurities such as anhydrite, calcium, magnesium, sulphate, and other minor impurities, is purified by adding carbonated cell liquor (produced on site by the flue gas from the power house reacting with caustic soda). The solids from the bottom of the saturator plus the purification solids from the clarifier are sent to a settling pond. The brine overflowing the clarifier is filtered and sent to a holding tank. This brine is then heated in a direct contact tower with hot hydrogen gas, resaturated with recovered salt from the caustic evaporator,

acidified, and then fed to the cells. Backwash from the brine filter also goes to the settling pond.

The hot, wet chlorine gas from the cells is cooled in indirect, water-cooled heat exchangers. The condensate is steam-stripped of chlorine and then recycled for salt dissolution. The chlorine is dried in a series of three sulphuric acid towers. The spent acid (about 60 to 70 percent H_2SO_4) is partially used for pH control of the final effluent. The remainder is sent to another plant for reuse. The dry chlorine is demisted, scrubbed with liquid chlorine, precooled, and compressed. The compressed gas is further liquefied first by using chilled water then liquid chlorine. The liquid chlorine is then stored for shipment.

The uncondensed chlorine gas from the liquefaction stage is burned with hydrogen to make hydrochloric acid for in-plant use. A sodium hypochlorite unit absorbs chlorine gas on startup and emergency situations and other waste gases, and also makes commercial hypochlorite for sale. Any excess is decomposed and discharged with the treated effluent.

The hot hydrogen gas from the cells is cooled by direct contact with the brine from the holding tank, compressed, and then either burned with chlorine to produce muriatic acid or used as fuel in the boiler house. Effluents from the HCl area drain into a tank and are from there pumped into the treatment system.

The cell liquor, which contains about 13 percent NaOH and 15 percent NaCl, is pumped to storage tanks. The water of this liquor is evaporated to a concentration of 50 percent NaOH. The liquor is cooled, filtered for final salt removal, and stored. About 70 percent of the evaporated water is collected and reused in the plant. The other 30 percent is picked up by the barometric condenser water which is recycled to the cooling towers. The crystallized salt is washed to remove sulphate and caustic. The first wash is recycled to the evaporator. The subsequent wash, a sulphate-rich brine, is treated to control its sulphate level and purged to the sludge-settling pond. The purified brine is recycled to the process. The washed salt crystals are returned to the head of the circuit to resaturate the brine.

Old asbestos diaphragm material is hosed off the cathode section in a special area. The slurry goes to a sludge pit. The asbestos that settles out is put in drums and buried. The effluent is filtered through a pressure filter. The effluent goes to the sludge pond. The asbestos cake is also placed in drums and buried.

Process wastewaters recovered both from the brine preparation and brine treatment area and from the caustic and salt recovery area are recycled and reused for salt dissolution, otherwise they are sent to the plastic-lined brine sludge pond.

Boiler blowdown, liquid waste flows both from the chlorine-handling and -storage areas and from the caustic storage and loading areas are collected and transferred to the treatment system for pH adjustment.

The cell liquor tanks, caustic storage tanks, sulphuric acid tanks, hypochlorite tanks, and fuel tanks are all contained within dykes. Accumulated wastewaters within the dyked area are analyzed and, if neutral, go to the ditch system; if not neutral, the effluent goes to the treatment system.

The ditch system drains the whole site of rainwater and receives cooling tower blowdown. Any spills not recovered by the process wastewater collection system drains into the ditch system. The effluent in the ditch is monitored for pH and conductivity; if pH correction is required, it is diverted to the effluent treatment system. If the salt level is high, the effluent is diverted to the sludge pond.

The treatment system is continuously monitored for pH. The treatment system is comprised of a retention basin followed by three interconnecting fibreglass (FRP) tanks, agitators, and pH meters. When the pH exceeds the acceptable limits, the effluent is neutralized by either the addition of cell liquor or the addition of sulphuric acid.

Sanitary wastewaters are connected to the sanitation sewers at the industrial site.

Total wastewater flows from this plant are monitored continuously. The data are presented in Table 19.

Plants No. 4 and 5

Plants 4 and 5 are on an integrated organic-inorganic chemical plant site. Saturated brine from brine wells is pumped to reaction tanks. In the reaction tanks, raw brine is purified by raising the pH of the brine with caustic soda and sodium carbonate produced on-site by treating caustic cell liquor with carbon dioxide. Heavy metals and magnesium are precipitated as hydroxides, and calcium as the carbonate.

The treated brine is filtered to remove the precipitates, heated, and then resaturated with salt recovered in the evaporation of caustic cell liquor, acidified with HCl, and then sent to the diaphragm cells. Backwash from the brine filter is recycled to the brine circuit. The brine purification solids are returned to the salt cavern.

TABLE 19 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 3, DIAPHRAGM CELL CHLOR-ALKALI PLANT

	FINAL EFFLUENT			
Parameters	No. of Values	Ave. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow* (m^3/d)		6200		
pH*	6	8.8	2.5-11.5	
Total Solids	6	1040	330-2300	12.9
Suspended Solids	6	10	5-24	0.12
Sulphate	6	24	12-50	0.30
Chloride	3	610	170-1000	11.1
Sodium	6	355	100-1000	4.4
Calcium	3	17	10-21	0.30
Magnesium	3	4	3-7	0.07
Iron	3	0.85	0.47-1.1	0.02
Chromium	3	0.42	0.33-0.48	0.008
Copper	3	< 0.03	<0.02-0.04	<0.0003
Nickel	3	< 0.02		<0.0002
Lead	3	< 0.02		<0.0002
Cadmium	3	< 0.01		<0.0001
Zinc	6	0.15	0.095-0.2	0.002
Cobalt	3	< 0.02		<0.0002
Arsenic	3	< 0.03		<0.0003
Residual Chlorine	3	< 0.05	0-80	

* Units in the column headings do not apply.

Cell room losses, which consist of spills, leaks, washdown waters, etc., are normally small; they are collected and recycled to the process. Wastewaters from the cell renewal area, which contains a high concentration of asbestos fibres, are sent to a lagoon. The wastewater is recycled to the process. The solids settle out and are periodically removed and buried at a company-owned, provincially approved landfill site.

Hot hydrogen gas from the new chlor-alkali plant is indirectly cooled, and the condensate is recycled to the plant. The older plant uses direct-contact cooling; the less

than 2 200 Lpm of cooling water, containing less than 0.1 g/L caustic, flows into the river. Most of the hydrogen gas is piped to an adjacent company.

The hot, wet chlorine gas from the cells is cooled by indirect cooling, dried by passing the gas through towers filled with progressively stronger sulphuric acid, compressed, purified, liquefied, and then stored. The condensate is shipped for use to another part of the plant complex. The spent sulphuric acid is dechlorinated and sold.

All waste chlorine gas streams that cannot be condensed, are sent to an alkaline brine scrubber. The hypochlorite produced is decomposed and recycled to the brine circuit.

The cell liquor, which contains about 12.5 percent caustic soda and about 13 percent salt is sent to evaporators to concentrate the sodium hydroxide to 50 percent. The caustic soda leaving the evaporators is cooled, filtered to remove sodium sulphate and other impurities, and then stored. Further purification to obtain some low-salt caustic soda is also undertaken. Salt, which crystallizes out of solution in the multi-effect evaporators, is recycled to the brine resaturators. The vapours from the evaporative concentration of caustic are cooled indirectly at these plants. All condensates are normally used in the plant; but if there is an excess, these waters with a conductivity of around 10 micromhos/cm are discharged to the river.

Chlorinated hydrocarbon wastes from the chlorine purification step are used as a feedstock for chemical manufacturing operations within the plant site.

A central facility treats all intake water for the entire site. This facility treats intake water with ferrous sulphate, lime, and polyphosphates, then passes it through filters and cation-and-anion exchange columns. Solids from this facility go to a lagoon. The liquid wastes from regenerating the ion exchange columns are treated and recycled.

Runoff wastewaters from both plants are collected and recycled. Sanitary wastes go to the city sanitary sewer.

The only process wastewater discharged from Plants 4 and 5 is a small amount of neutralized spent sulphuric acid, some condensate from the caustic evaporators with a conductivity of around 10 micromhos/cm, and some direct-contact cooling water used to cool the hydrogen gas from the older chlor-alkali plant. No analysis of the wastewater from the combined plants was available.

Plant No. 6

At Plant 6, which is on an integrated organic-inorganic chemical plant site, brine from brine wells, containing calcium, magnesium, sulphate, and other minor

impurities is pumped to treatment tanks. In the tanks, the brine is purified by adding sodium carbonate. The sodium carbonate is produced at the plant by having cell liquor react with flue gas and caustic soda. Heavy metals and magnesium are precipitated as hydroxides, and calcium as the carbonate.

The treated brine is filtered to remove the precipitated solids, heated, and resaturated with salt recovered from the caustic evaporators. The resaturated brine is acidified and then sent to the cells. The brine purification solids are sent to a deep well. Any water associated with brine purification, such as brine filter backwash, spills, washup, etc., is recycled to the process.

Cell room losses, which consist of spills, leaks, washdown, etc., are collected and recycled to the process. The cell renewal wash waters, heavily laden with asbestos fibres, are settled in a clarifier. The water is recycled to the process and the solids are pumped to a salt cavity with the approval of the Provincial Government agency.

The hot, moist chlorine gas from the cells is cooled and dried, and then either compressed, purified, liquefied and stored, or piped to other parts of the plant complex for use. The condensate is pumped to another part of the plant complex and used. The spent sulphuric acid is neutralized and discharged to a deep well with the approval of the Provincial Government agency.

The hot hydrogen gas is cooled directly. The condensate is recycled. Part of this hydrogen gas is used to produce HCl which is used on-site or sold. Wastewaters discharged from these units are recycled to the process.

Most of the waste chlorine gas streams that cannot be condensed are sent to the tailgas HCl burners, and then to backup alkaline scrubbers. Effluents from these scrubbers is recycled to the process.

The cell liquor, which contains about 13 percent caustic soda and an equivalent amount of salt, is sent to evaporators to concentrate the sodium hydroxide to 50 percent. The caustic soda leaving the evaporators is cooled, filtered to remove sodium sulphate and other impurities, and then stored. Salt, which crystallizes out of solution in the evaporators, is recycled to the brine circuit. The vapours from the evaporators, after non-contact cooling, are reused in the plant.

A central facility treats all intake water required for the integrated plant site. Conventional treatment such as coagulation, flocculation, and filtration followed by ion exchange softening is used.

Wastes from these units go to a lagoon for settling out the solids and pH adjustment before being discharged to the river.

Chlorinated hydrocarbon wastes from the chlorine purification step are used as feedstock for chemical manufacturing operations within the plant site. Process wastewater from these manufacturing operations are steam-stripped to remove volatile organics, followed by neutralization, and then treatment in a bio-oxidation unit to remove non-volatile organics from water.

Plant runoff wastewaters are collected, treated and reused.

Cooling towers provide cooling water for the integrated plant site. Blowdown from these units is treated and then discharged into the river.

Sanitary effluent is sent to secondary treatment facilities.

The company claims that there is no wastewater flow from the chlor-alkali plant, thus no analysis table has been compiled. The alkaline streams are collected, neutralized, and then sent to an effluent recycling pond, where further treatment takes place before the water is recycled to the process.

Off-spec brine is collected from cell washers during start-up and shut-down, and blended into the raw brine flow.

3.4 Priority Pollutants and Biological Testing - Methodology

3.4.1 Priority Pollutants. By screening and verification sampling programs the Environmental Protection Agency established the presence of some of the 129 listed pollutants in effluent from diaphragm cell plants. Factual information was derived from the chemical analysis and flow measurements of representative process raw wastewater streams and treated effluents. The data collected are shown in Tables 20 and 21.

The presence of any of the 129 listed priority pollutants in final effluent from diaphragm cell plants in Canada was established by sampling three of the seven operating plants, using the procedures outlined in Section 2.4.

Factual information was derived from chemical analysis and flow measurements of representative final effluent from plants in this category.

i) Metals

None of the priority metals were found in significant concentrations at diaphragm cell plants. The amount of metals shown in Table 22 in the final effluent from these plants includes both the background contribution and the contribution from the plant itself. Since the concentrations are too low to be treatable by conventional techniques (e.g., chemical precipitation), they are not considered further.

TABLE 20 SUMMARY OF RAW WASTE LOADINGS AT SCREENING AND VERIFICATION METAL ANODE PLANTS IN THE U.S.A.[1]

SUBCATEGORY	CHLORINE DIAPHRAGM CELL			
	Unit Loading (kg/kkg)			Number of Plants*
Pollutant	Minimum	Average	Maximum	Average (out of 5)
Antimony	0.0000033	0.0000033	0.0000033	1
Arsenic	0.0000064	0.000017	0.000030	3
Cadmium	0.0000014	0.0000032	0.0000061	3
Chromium	0.000017	0.00096	0.0046	5
Copper	0.000014	0.00020	0.00064	5
Lead	0.0000039	0.00016	0.00060	5
Mercury	0.0000007	0.0000012	0.0000018	2
Nickel	0.000010	0.00057	0.0018	5
Silver	0.0000017	0.0000007	0.0000007	1
Zinc	0.000054	0.00078	0.0021	4

* Only those plants where the pollutant was observed at measurable concentrations.

Asbestos, used as a diaphragm for separating the anodes and cathodes, is one of the major priority pollutants found in process wastewaters from diaphragm cell plants.

Effluent from only one plant was analyzed for asbestos. The total fibres per liter count was 0.27and 0.81 million fibres; however, the analysis for asbestos was complicated by the presence of other fibres. The latest U.S.A. epidemiologic study of asbestos in drinking water, cancer incidence, and cancer mortality does not implicate waterborne asbestos as a carcinogen.

ii) Organic Pollutants

The samples were collected and analyzed by the methods described in Section 2.4.

TABLE 21 RAW WASTE TOXIC ORGANICS AT A GRAPHITE ANODE PLANT IN THE U.S.A.

SUBCATEGORY	CHLORINE DIAPHRAGM CELL	
	Concentration* (mg/L)	Load (kg/day)
benzene	0.00040	0.0011
carbon tetrachloride	0.023	0.066
1,2-dichloroethane	0.079	0.23
1,1,1-trichloroethane	0.00014	0.00040
hexachloroethane	0.010	0.029
1,1,2-trichloroethane	0.00040	0.0011
1,1,2,2-tetrachloroethane	0.000044	0.00013
chloroform	0.085	0.24
1,1-dichloroethylene	0.000026	0.000074
2,6-dinitrotoluene	0.000026	0.000074
methylene chloride	0.00056	0.0016
bromoform	0.000063	0.00018
dichlorobromomethane	0.035	0.10
chlorodibromomethane	0.002	0.0057
hexachlorobutadiene	0.004	0.011
bis(2-ethylhexyl)phthalate	0.00075	0.0022
di-n-butyl phthalate	0.00078	0.0022
tetrachloroethlene	0.036	0.10
toluene	0.0030	0.0086
trichloroethylene	0.020	0.0057

* Flow-proportioned concentration

3.4.2 Aquatic Toxicity Testing. Large samples of final effluent from two diaphragm cell plants were collected for acute toxicity testing. The reasons for carrying out aquatic toxicity testing are outlined in Section 2.4.2.

3.4.3 Biological Testing. The materials and methods used to test the final effluent from diaphragm cell plants for genotoxic activity are outlined in Section 2.4.3.

TABLE 22 SUMMARY OF PRIORITY METAL CONCENTRATIONS AND LOADINGS IN FINAL EFFLUENT FROM DIAPHRAGM CELL PLANTS

Pollutant	CONCENTRATION		DAILY LOADINGS		UNIT LOADINGS	
	Average (mg/L)	Maximum	Average (kg/day)	Maximum	Average (kg/kkg)	Maximum
Cadmium	<0.001	<0.01	<0.072	<0.08	<0.00014	<0.00018
Chromium	0.18	0.42	1.38	2.60	0.0043	0.008
Copper	0.02	0.04	0.46	0.73	0.0023	0.005
Nickel	0.01	0.01	0.35	0.82	0.0015	0.0018
Lead	<0.010	<0.02	<0.38	<0.65	<0.008	<0.0014
Antimony	<0.008		<0.65	<0.65	<0.0014	
Zinc	0.10	0.15	2.92	4.92	0.006	0.011
Mercury	0.0002		0.016	0.016	0.000036	
Arsenic	<0.03		<0.18	<0.18	<0.0003	
Asbestos	0.54 M fibres/L					

3.5 Discussion of Results

3.5.1 Conventional Pollutants. As outlined for mercury cell plants, the parameters - pH, suspended solids, and residual chlorine - also showed wide ranges in concentrations in final effluent from the three diaphragm cell plants discharging process wastewaters (Tables 17, 18, and 19).

Normally, the pH of the final effluent is within the range of 6 to 9; however, excursions from around 2 to 12.5 do occur. These plants adjust the pH through controlled additions of acid or alkali. Better control, however, could be achieved, if adequate retention were provided to attain complete equilization.

The concentration of suspended solids from diaphragm cell plants is normally low as the solids from brine treatment are either directed to a pond or returned to salt cavities, and cell room solids (mainly used asbestos) are disposed of at authorized landfill sites.

At two plants, where the final effluent is discharged into the sea, the solids from brine treatment are discharged at a controlled rate. These solids are inert and non-toxic, and as the amounts of solids being discharged are quite low; little, if any, detrimental environmental impact results from this practice.

Residual chlorine levels in the final effluent from most plants is normally zero; however, wide fluctuations (from 0 to 80 mg/L) do occur. Because of the toxicity of low levels of chlorine in wastewaters, dechlorination treatment should be practiced. Chlorine residuals after the recovery or decomposition, or both, and recycling steps noted in Section 3.4 would be amenable to treatment with reducing agents such as sulphur dioxide or hydrogen peroxide, particularly if adequate retention time is provided.

3.5.2 Priority Pollutants and Biological Testing

i) Organic Pollutants

The priority organic pollutants found in diaphragm cell plant effluent (Table 23) are not acutely or chronically toxic to either fresh-water or salt-water aquatic life, since their concentrations are very low.

ii) Aquatic Bioassay

The final effluent from Plant No. 1 was non-toxic to fish at 100-percent concentration over a 96-hour period. The final effluent from Plant No. 3 was quite alkaline -a pH of 11. When the pH was reduced to 7.5, the effluent was non-toxic at 100-percent concentration over a 96-hour period.

TABLE 23 PRIORITY ORGANIC POLLUTANTS FOUND IN DIAPHRAGM CELL CHLOR-ALKALI PLANTS FINAL EFFLUENT, THEIR CONCENTRATION RANGE AND AMBIENT WATER QUALITY CRITERIA PROPOSED BY EPA (USA)

Parameter	Levels found in C-A Effluent (ug/L)	Proposed EPA Criteria[1]				
		Freshwater Aquatic Life (ug/L)		Saltwater Aquatic Life (ug/L)		Human Health
		Acute	Chronic	Acute	Chronic	(Estimated)
Chloroform	2-14	28 900	1 240	-	-	
Carbon Tetrachloride	2-7	35 200	-	50 000	-	
1,2-Dichloroethane	T-7	118 000	20 000	113 000	-	
Trichloroethylene	T-1	45 000	-	2 000	-	
Bromodichloromethane	T-28	11 000	-	12 000	6 400	
Toluene	T-2	17 500	-	6 300	5 000	14.3 ug/L
1,1,1-Trichloroethane	T-3	18 000	9 400	31 200	-	18.4 ug/L
1,2-Dichloropropane	0-30	23 000	5 700	10 300	3 040	
Trans-1,3-Dichloropropene and cis	0-3	6 060	244	790	-	87 ug/L
Dichloromethane	T-4	224 000	-	-	-	
Bromoform	0-127	29 300	6 400	24 400	-	
Diethylphthalate	2-6	52 100	-	7 590	-	350 mg/L
Dibutylphthalate	4-31	940	-	-	-	34 mg/L
Di(2 ethylhexyl)phthalate	0-8	11 100	< 3	-	-	15 mg/L
Tetrachloroethylene	T	5 280	640	10 200	450	
Benzene	T-6	5 300	-	5 100	700	
Phenol	0-4	10 200	2 560	5 800	-	3.5 mg/L
Chlorodibromomethane	0-20	11 000	-	12 000	6 400	

1. From EPA "Ambient Water Quality Criteria" Reports.
T = Trace

iii) Biological Testing

Only one final effluent sample from diaphragm cell chlor-alkali plants was tested for genotoxic activity using a battery of four short-term bioassays. (Effluent from another diaphragm cell plant was tested for genotoxic activity; however, this sample contained effluent from other organic plants as well as chlor-alkali effluent, thus it is not included in this report.)

The straight effluent was tested for mutagenicity in Salmonella typhimurium using a suspension test procedure. The concentrated extract prepared from the sample was tested for its capacity to induce mutations in Salmonella, chromosome aberrations in Chinese hamster ovary cells, DNA damage and inhibitions of DNA repair in cultured human fibroblasts.

No mutagenic activity was demonstrable with the straight effluent in the Salmonella mutagenicity test over the dose range tested.

Mutagenic activity was detected in the effluent extract using the Salmonella mutagenicity test. This extract yielded a two-fold increase in strain TA 100 without the liver enzyme-activation system. When S-9 (the liver enzyme-activation system) was added, only a dose-related increase in colony count, but not reaching two-fold above background, was obtained. It would appear that the liver enzyme activity altered the compounds in question. The alteration resulted in loss of mutagenic activity; the mutagenic compounds may have been metabolized to a predominately non-mutagenic form. No mutagenic activity was demonstrable with the extract blank whether S-9 was included or not.

No damage to chromosomes in Chinese hamster ovary cells was demonstrable with or without S-9 for the sample extract.

No DNA repair was demonstrable in cultured human fibroblasts for the sample extract.

The sample extract exhibited no DNA repair inhibition with or without the addition of S-9.

The results of this study are summarized in Tables 24 and 25. For further details one is referred to Tables C1 to C6 in Appendix C.

3.5.3 Discussion. Most of the toxic chlorinated organic pollutants found in mercury cell chlor-alkali plant effluent were also present in diaphragm cell plant effluent at about the same concentrations. Thus the comments made in Section 2.6.3 also apply to diaphragm cell plants.

TABLE 24 SUMMARY OF TESTING OF EFFLUENT SAMPLES

EFFLUENT CODE NO.	STRAIGHT EFFLUENT		EXTRACT							
	SALMONELLA MUTAGENICITY		SALMONELLA MUTAGENICITY[a]		CHROMOSOME ABERRATION[b]		DNA REPAIR[c]		DNA REPAIR INHIBITION[d]	
		+S-9		+S-9		+S-9		+S-9		+S-9
1	-	-	+	±	-	-	-	-	-	-

[a]Salmonella mutagenicity:
+ = positive: colony count reaching at least twofold increase above background.
± = dose-related increase in colony count but not reaching twofold above background.
- = negative: neither dose-related nor twofold increase in colony count above background.
[b]Percentage of metaphases with chromosome aberrations: - = 0-4%; + = 5-9%; + = ≥10%.
[c]Maximum mean grains per nucleus observed: - = 0-4; ± = 5-9; + = >10.
[d]DNA repair inhibition: + = inhibition observed; - = inhibition not observed.

TABLE 25 SUMMARY OF SALMONELLA MUTAGENICITY TEST RESULTS

EFFLUENT CODE NO.	STRAIGHT EFFLUENT					EXTRACT				
	1535	100	1537	1538	98	1535	100	1537	1538	98
	+S-9	+S-9	+S-9	+S-9	+S-9	+S-9	+S-9	+S-9	+S-9	+S-9
1	- -	- -	- -	- -	- -	- -	+2 ±	- -	- -	± ±

+ = positive: colony count reaching at least twofold increase above background. Number indicates fold increase in mutant colony count above background.

± = dose-related increase in colony count but not reaching twofold above background.

- = negative: neither dose-related nor twofold increase in colony count above background.

In addition to the many chlorinated organics, bromoform and dibromochloromethane were also present in the diaphragm cell plant effluent. Bromoform has been shown to be mutagenic only when tested in desiccators, but not when incorporated into agar and tested with Salmonella typhimurium, as was done at the B.C. Cancer Research Centre.

The final effluent from the diaphragm cell plant contained known mutagens and carcinogens as well as many potential mutagens/carcinogens; however, no genotoxic activity was evident, when the straight effluent was tested using the Ames test, and only a two-fold increase of mutagenic activity in strain TA 100 without the liver enzyme-activation system, and less than a two-fold increase when S-9 was added.

The analysis of mutagenicity of wastewaters is complicated by many technical problems:

(i) Discrepancies arise among the bioassays from differences in their sensitivity and applicability to various classes of chemicals and differences among investigators in experimental protocols and techniques of data analysis and interpretation.

(ii) Wastewaters, like any complex environmental sample, may contain mutagenic substances in a matrix of innocuous and toxic substances, and

(iii) in some cases, mutations may have been induced as the result of synergism between two or more compounds with individual concentrations possibly too low to induce reversion alone; whereas in other cases, where only one mutagenic compound is present in wastewaters, the concentration might be too low to induce reversion alone. Consequently, a clear mutagenic response and a linear dose-response curve as one generally finds with pure compounds may not be seen.

In addition to the many technical problems that arise, the genotoxicity test data for diaphragm cell plants are based on an isolated effluent sample and thus are inadequate for the assessment of possible human health hazards and other environmental impacts. In assessing the impact that wastewaters from chlor-alkali plants have on the environment, other factors must also be taken into consideration; e.g., dilution of the effluent upon its entry into receiving waters, the possibility of the effluent entering drinking-water supplies, the fate of the toxic pollutants (bioaccumulation, volatilization, sorption, etc.), and fluctuations in the release of toxic pollutants from a plant.

3.6 Pollution Abatement Options and Treatment Technology

3.6.1 Conventional Pollutants. In-plant process modifications have significantly reduced pollutant loads discharged from chlor-alkali plants. Such modifications include:

- segregation of contaminated wastewaters from relatively clean wastewaters,
- recycling of as much contaminated wastewater as practical, and
- treatment of the remaining wastewaters.

These modifications have reduced conventional pollutant loadings as well as priority pollutant discharges. Other in-plant modifications which will help to reduce pollutant loading in wastewater discharges include the following:

Anode Material

Three of the six plants use dimensionally stable anodes rather than graphite anodes. The type of anode used at the other three plants was not disclosed. The use of dimensionally stable anodes increases current efficiency, greatly reduces the pollutant load of toxic organics present in plant wastewater, and produces cell gas of higher purity which along with the use of refrigeration units for chlorine recovery reduces the amount of gas vented from the chlorine liquefaction system.

Lead normally occurs in high concentrations in cell-room wastewaters from chlorine plants using graphite anodes.

Irrespective of the type of anode used in the three plants that did not reveal the type of anode used, it was disclosed that no lead is used to provide electrical contact and support (thus no lead should be present in the cell wastewaters), and all chlorinated organic impurities from the chlorine reboiler are used as feedstock for the manufacture of similar products within the plant site.

Tail Gas Emission Control

As with mercury cell plants, chlorine in tail gases has to be removed or recovered before it is vented to the atmosphere. At all plants the gas is scrubbed with caustic soda. The sodium hypochlorite thus produced is then sold, used on site, or decomposed and recycled, or discharged. Chemical or catalytic decomposition methods are used.

Chlorine Condensates and Spent Drying Acid

The comments noted for mercury cell plants also apply to diaphragm cell plants. At two diaphragm cell plants, the chlorine condensate is sent to an adjacent plant on the same site.

Caustic Evaporation Water

The vapours from the evaporative concentration of caustic soda are cooled in surface condensers at three plants and through barometric condensers at the other three plants. By using non-contact cooling or by recirculating water from barometric condensers, the amount of wastewater generated can be considerably reduced.

At one plant using barometric condensers, the condenser water is recycled to the cooling towers. At the other two plants using barometric condensers, the coolant is seawater, thus any salt and caustic carryover in the vapour has little effect on the composition of the seawater.

Asbestos

Asbestos wastes are stored in ponds and subsequently sent to landfill sites or filtered, stored in drums, and then sent to a landfill site.

Since asbestos wastes are completely insoluble in a landfill, the recommended procedure of disposal is filtration, storage in drums, or settling in ponds followed by disposal in an authorized landfill site. The effluent from this operation should be recycled or reused.

Other measures, besides these in-plant control practices, are usually required for further treatment of the wastewater streams. In general, these streams may be divided into cooling water and process wastewater.

Any once-through cooling water should be relatively free of suspended solids and dissolved salts, except when seawater is used for cooling. Any contaminants added would come from leaks which should be detected with monitoring equipment (if fresh-water is used for cooling). Aciditiy and alkalinity are detected by pH meters, often installed for continuous metering and control. Concentrations of dissolved solids can be estimated by conductivity measurements, suspended solids by turbidity, and specific ions by colorimetric measurements or by using ion-specific electrodes.

In any event, contaminants present in once-through cooling water should be very low, and treatment should not be required. On the other hand, process wastewaters do require treatment.

Suspended solids, dissolved solids, pH, and residual chlorine are the major conventional parameters that could be of concern in the production of caustic-chlorine by the diaphragm cell process.

Brine purification muds constitute the major source of solid wastes generated at these plants. Settling ponds or vessels are the major techniques used for reducing the concentration of suspended solids in wastewater streams from the plant. Their performance and cost depend on both the amount of waste involved and the settling characteristics of the solids suspended. Purity of the raw material used in the manufacturing process, of course, influences the waste load. The economics of raw--material purity need to be balanced against the attendant waste treatment and disposal costs.

Other sources of suspended solids coming from the plant include solid wastes removed from incoming surface water, and materials (concrete, asbestos fibres, etc.) from rebuilding electrolytic cells. These solids settle out in ponds or go to authorized landfill sites, or both.

Most of the chlor-alkali wastewaters are either acidic or alkaline or react with water to give acidic or alkaline solutions. Before disposal in surface waters, this acidity or alkalinity needs to be reduced and controlled. Control of excess acidity or alkalinity is best accomplished by taking advantage of available acid waste streams to neutralize basic waste streams and vice versa, and also by pH monitoring. If no holdup facilities are available, wide fluctuations in pH can occur (Tables 17, 18 and 19).

Residual chlorine concentrations are normally non-detectable or below 0.1 mg/L. Periodic high values, however, do occur normally during plant start-ups, upsets, or when undetected leaks occur. These discharges are of concern due to the fact that chlorine in very low concentrations is toxic to fish, and the interaction between residual chlorine and soluble organic compounds may lead to the formation of chlorinated hydrocarbons.

Dechlorination may be carried out by reacting chlorinated solutions with sodium sulphite, sodium metabisulphite, or sulphur dioxide. Dechlorination with sulphur dioxide appears to be the most economical and accepted method. The reaction is almost instantaneous and should be satisfactory for in-line applications, where the concentration of residual chlorine is fairly constant. Where high concentration peaks occur, a hold-up system is required to equilize the concentration.

At two plant sites, where salt solution mining is used and salt cavities or deep wells, or both, are available, an ideal situation exists in that no process wastewaters are discharged, instead most of the process wastewaters are recycled and reused, and the slurry brine treatment solids is discharged into a deep well or salt cavity. In addition,

some condensates are reused in other plants on the integrated plant site. Zero discharge may not be achieved without the use of salt cavities, deep wells, or evaporation ponds.

3.6.2 Priority Pollutants. Asbestos used as a diaphragm separating the anode from the cathode is likely to be the major priority pollutant consistently found in process wastewaters from these plants. The best practical technological method of removing asbestos fibers from the cell-room washdown and cell maintenance wastewaters is confinement followed by settling in ponds or filtration. The solids should be placed in an authorized landfill site. Since the fibers are in the micron size, flocculating agents should be used and all wash-waters should be recycled or reused.

Dimensionally stable anodes are used at three plants, and no lead is used at the other three plants, thus high concentrations of lead are not present in any effluents from Canadian diaphragm cell plants. In fact, all metal concentrations were below the most practical treatability levels.

Priority organic pollutants were found to be present in measurable amounts in the final effluents. Table 26 presents a list of the concentrations of various compounds found. This table also shows the aquatic fate of these contaminants and lists the best treatment methods to remove these contaminants from wastewaters.

Individual waste streams were not monitored for priority pollutants, thus the point of origin of these pollutants within the plant was not established. Treatment methods used to remove chlorinated organics from the effluent of the entire plant would be too costly for most plants for the probable benefits obtained, since the significance of low concentrations of the priority pollutants found in the final effluent has not yet been established.

If the need arises, the individual streams should be monitored for chlorinated hydrocarbons. If certain streams contain the bulk of the priority pollutants, then some effort should be made to remove them using one of the treatment methods noted in Table 26.

It might well be that the problem could be eliminated or greatly reduced by the installation of dechlorination equipment, if residual chlorine reacting with soluble organics present in the wastewaters is, in fact, responsible for the formation of most of the priority pollutants found.

3.6.3 Selection of Appropriate Technology. Three diaphragm cell plants would be classified as exemplary plants, since one plant discharges no process wastewater and the

TABLE 26 PRIORITY ORGANIC POLLUTANTS FOUND IN FINAL EFFLUENT FROM DIAPHRAGM-CELL CHLOR-ALKALI PLANTS AND THEIR AQUATIC FATE AND POSSIBLE TREATMENT METHODS

PARAMETER	LEVELS FOUND IN C-A EFFLUENT (ug/L)	AQUATIC FATE[1]					Treatment[2]
		Photolysis	Hydrolysis	Volatilization	Sorption	Bioaccumulation	
Chloroform	2-14	Probably not significant	Probably not significant	Primary transport process	Probably not significant	Weak to moderate	Steam stripping and activated carbon adsorption considered best
Carbon Tetrachloride	2-7	Probably not significant	Too slow to be significant process	Primary transport process	No clear evidence of selective conc'n in sediments	Inconclusive	Gas flotation, GAC adsorption and sedimentation with alum and lime addition
1,2-Dichloroethane	T-7	Appears to be insignificant	Probably too slow to be significant	Primary transport process	Probably not important	Probably not significant	Sedimentation with alum and polymer addition
Trichloroethylene	T-1	Probably does not occur	Probably too slow to be significant	Primary transport process	Probably not important	Evidence of some accumulation by marine organisms	Gas flotation, activated sludge. GAC adsorption and reverse osmosis
Bromodichloromethane	T-28	No information found	Too slow to be significant fate	No specific info. Probably serves as significant transport	No specific info.	May bioaccumulate	Gas flotation with alum and polymer addition or GAC adsorption
Toluene	T-2	Direct photolytic cleavage is energetically improbable	Not significant	Significant process	Cannot be determined	Probably not important	Biological degradation, GAC adsorption and steam stripping or aeration
1,1,1-Trichloroethane	T-3	Probably not significant	Probably occurs too slowly to be significant	Primary transport process	Probably not important	Probably not important	Activated sludge (likely due to stripping) and carbon adsorption
1,2-Dichloropropane	0-30	No data	No data, probably important	Compound volatile but may return through precipitation	No data, may be adsorbed moderately	No data, may bioaccumulate slightly	Activated sludge and GAC adsorption
Trans-1,3-Dichloropropene and cis	0-3	No data	Appears to be slow, but may be important	Primary transport process	No data	No data, probably not important	Biodegradation
Dichloromethane	T-4	Probably not significant	Probably not a significant fate	Primary transport process	Probably not significant	Probably does not significantly bioaccumulate	Sedimentation with alum addition or gas flotation with alum addition

TABLE 26 PRIORITY ORGANIC POLLUTANTS FOUND IN FINAL EFFLUENT FROM DIAPHRAGM-CELL CHLOR-ALKALI PLANTS AND THEIR AQUATIC FATE AND POSSIBLE TREATMENT METHODS (CONT'D)

PARAMETER	LEVELS FOUND IN C-A EFFLUENT (ug/L)	AQUATIC FATE[1]					Treatment[2]
		Photolysis	Hydrolysis	Volatilization	Sorption	Bioaccumulation	
Bromoform	0-127	No information	Too slow to be significant	Little info. may serve as significant transport process	No information	Bioaccumulation in organisms may be possible	Powdered activated carbon adsorption
Diethylphthalate	2-6	Probably does not undergo direct photolysis	Not considered a competitive process	Not as important as adsorption	Sorption onto S.S. and biota probably most important	Considered an important fate process	Sedimentation with chemical addition and activated sludge
Dibutylphthalate	4-31	Probably does not undergo direct photolysis	Not considered a competitive process	Not as important as adsorption	Sorption onto S.S. and biota probably most important	An important fate process	Gas flotation with chemical adddition, sedimentation with chemical addition and GAC
Di(2 ethylhexyl)phthalate	0-8	Probably does not undergo direct photolysis	Will hydrolyze slowly not a competitive process	Not as important as adsorption	Probably most important transport process	An important fate process	Sedimentation with chemical addition, aerated lagoons and powdered activated carbon
Tetrachloroethylene	T	Probably does not occur	Probably occurs too slowly to be significant	Primary transport process	Probably not important	Evidence of bioaccumulation by marine organisms but not up food chain	Gas flotation with alum and polymer, sedimentation with alum or lime, activated sludge
Benzene	T-6	Probably not significant	Probably not significant	Probably primary transport process	No information may occur	Likely low bioaccumulation potential	Aerated lagoon, R.O. or gas flotation with polymer
Phenol	0-4	May be important degradation process	Not relevant	Possibility	Not a significant process	Not a significant process	Gas flotation with polymer, sedimentation with lime or polymer or alum, GAC adsorption or R.O.
Chlorodibromomethane	0-20	No information	Too slow to be significant	Probably serves as a significant transport process	Adsorption onto activated carbon probably significant	May bioaccumulate	Sedimentation with chemical addition

1. From EPA "Water-Related Environmental Fate of 129 Priority Pollutants".
2. From EPA "Treatability Manual" Volume 1.

other two plants discharge only minor amounts of relatively clean process wastewaters. Most chlor-alkali plants in Canada, however, do not have salt cavities, deep wells, or large holding facilities in areas with light rainfall, and so they must discharge larger quantities of process wastewaters.

For these reasons the following technology is recommended:

i) Solids from the brine saturator and treatment solids should be filtered from the brine and then washed to remove residual brine or sent to lined ponds for settling. The weak brine, filtrate, and wash waters should be recycled to the process. The solids should be sent to landfill.

ii) Cell wash waters, laden with asbestos, should be treated by the addition of flocculating agents, and then filtered through pressure filters or sent to a lined pond. In either case the solids should be sent to an authorized landfill site, and the wastewaters recycled.

iii) Cell room wastes consisting of leaks, spills, and area washdown, which might contain priority metals, should be recycled to the process.

iv) Tail gas scrubber solutions should be sold, used, or decomposed and recycled to the brine circuit.

v) Spent sulphuric acid should be regenerated for reuse, sold, used for pH control of the final effluent or neutralized before discharge.

vi) Other process wastes such as caustic filter backwash, chlorine bearing wastes, cooling tower blowdown, water treatment waste, boiler blowdown, storm runoff, etc. should be combined in a holding pond, adjusted for pH, dechlorinated, and then discharged after maximum recycling or reuse, or both.

4 MEMBRANE CELL PROCESS

4.1 Membrane Cell Process Description.

In the ion-exchange membrane process, a cation-exchange membrane is used as the partition between an anode compartment and a cathode compartment to prevent hydroxyl (OH^-) ions in the cathode compartment from migrating into the anode compartment. The cation-exchange membrane also prevents chlorine (Cl^-) ions from transferring from the anode compartment to the cathode compartment, while allowing sodium (Na^+) ions to migrate from the anode compartment into the cathode compartment. (Figure 5 shows a schematic of the membrane compartment and cell arrangement).

The Hooker MX cell, used at Dryden, resembles a filter press with multiple cells. Each cell contains an anode compartment with a dimensionally stable anode and a cathode compartment. One or more flat ion-exchange membranes, about one square meter in size, separate the two compartments. Individual cells are electrically connected in series.

In the MX cell, saturated brine and pure water are fed to the cell. At the anode, chloride ions lose an electron to become chlorine gas. At the cathode, hydronium ions (present with hydroxyl ions in water) gain an electron to form hydrogen and water, leaving a basic sodium hydroxide solution. The electrical circuit is completed by positive sodium ions flowing through the membrane from anode to cathode compartment. A small number of chloride ions does pass through the cathode compartment; however, this can be drastically reduced by using two membranes.

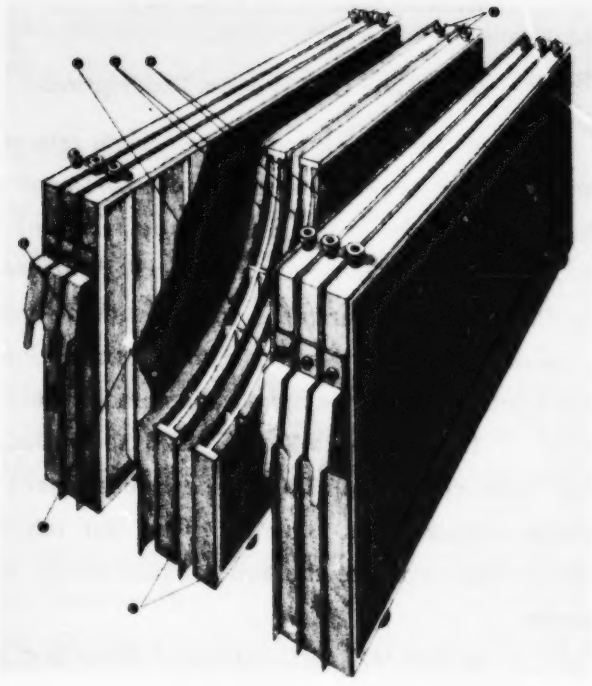
The Asahi cell, which is used at two other plants in Canada, is a bipolar type composed of many frames. The anode compartment is covered by titanium, and the cathode compartment is formed of steel. All the components of both compartments are made of metal so the cell can be operated at a temperature of 90°C without causing corrosion. Therefore the heat, generated during electrolysis, can be recovered for the evaporation of water from the caustic soda solution.

The ion-exchange membrane, which has an effective area of about 2.7 m^2 is installed between the anode and cathode compartments.

Adjacent anodes and cathodes are installed strictly in parallel about 2 to 3 mm apart. One electrolyzer has about 80 bipolar electrodes assembled in a single frame, and has the capacity to produce 10,000 tonnes per year of caustic soda.

LEGEND:

1 Cell frames
2 Titanium-steel compositive plate
3 Anode
4 Cathode
5 Rib of compartment
6 Supporting arms
7 Ion-exchange membrane



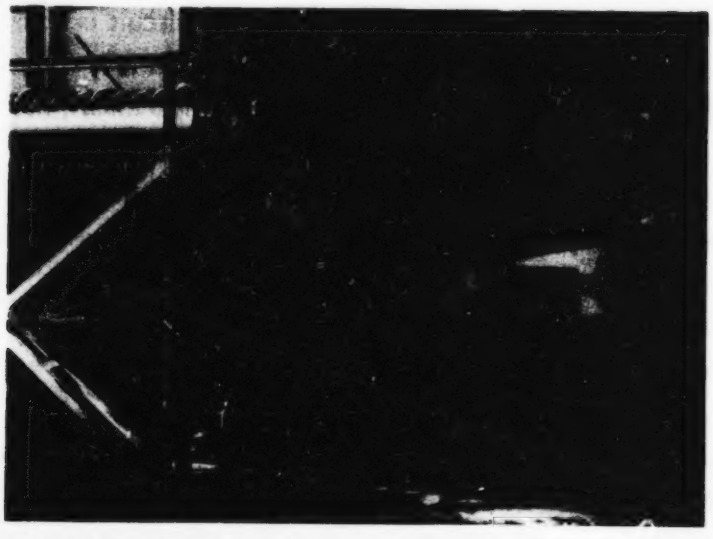


FIGURE 5 SCHEMATIC DIAGRAM OF MEMBRANE CELL COMPARTMENT AND ARRANGEMENT OF CELL (Taken from the Asahi Chemical Membrane Chlor-Alkali Process Information Booklet).

Saturated salt solution is passed through a brine pre-treatment system followed by an ion-exchange resin bed to remove multivalent cations. The saturated salt solution is then supplied to the anode compartment (Figure 6). Sodium ions migrate through the cation-exchange membrane to the cathode side. The sodium ions, together with hydroxide ions generated from water at the cathode, form sodium hydroxide. Pure water is injected into the catholyte stream to maintain a certain concentration of catholyte. A part of the catholyte stream (NaOH at a concentration of about 21 percent) is sent from the catholyte tank to the adjacent pulp and paper plants as is, or to the heat recovery evaporator for concentration. Chlorine gas is generated at the anode and used in adjoining plants or is liquefied and stored for later sale.

4.2 Water Use and Wastewater Sources

4.2.1 Water Use. Uses of water in membrane cell plants are similar to the needs mentioned for diaphragm cell plants: non-contact cooling, tail gas scrubbers, cell washing, brine circuit, general housekeeping, filter backwash, and for the barometric condenser. Unless non-contact cooling is employed, or the condenser water is recycled, only the blowdown make-up water is required. In addition, pure water must be added to the catholyte tank as well as water required for the deionizer and demineralizer.

4.2.2 Waste Sources

Dissolver Slurry

Only one plant uses rock salt as the raw material for brine makeup. Solids from the dissolver tank are filtered and sent to a large clarifier used to treat the effluent from the pulp and paper process. Solids from this clarifier are shipped to an authorized landfill site. The other two plants use brine wells and evaporated salt.

Brine Mud

At one plant closed-circuit brine wells are used, thus all solids from brine treatment and filter backwash are sent to the salt cavity. At another plant evaporated salt is used, thus the quantity of brine sludge and filter backwash is low. This effluent stream goes to a holding pond. At the third plant, brine purification solids from the clarifier underflow are filtered and sent to the pulp and paper clarifier. The backwash from the filters is used to slurry the brine solids for pumping to the clarifier.

The amount of brine sludge and filter backwash discharged range from 0.01 to 0.15 m^3 per tonne of chlorine produced.

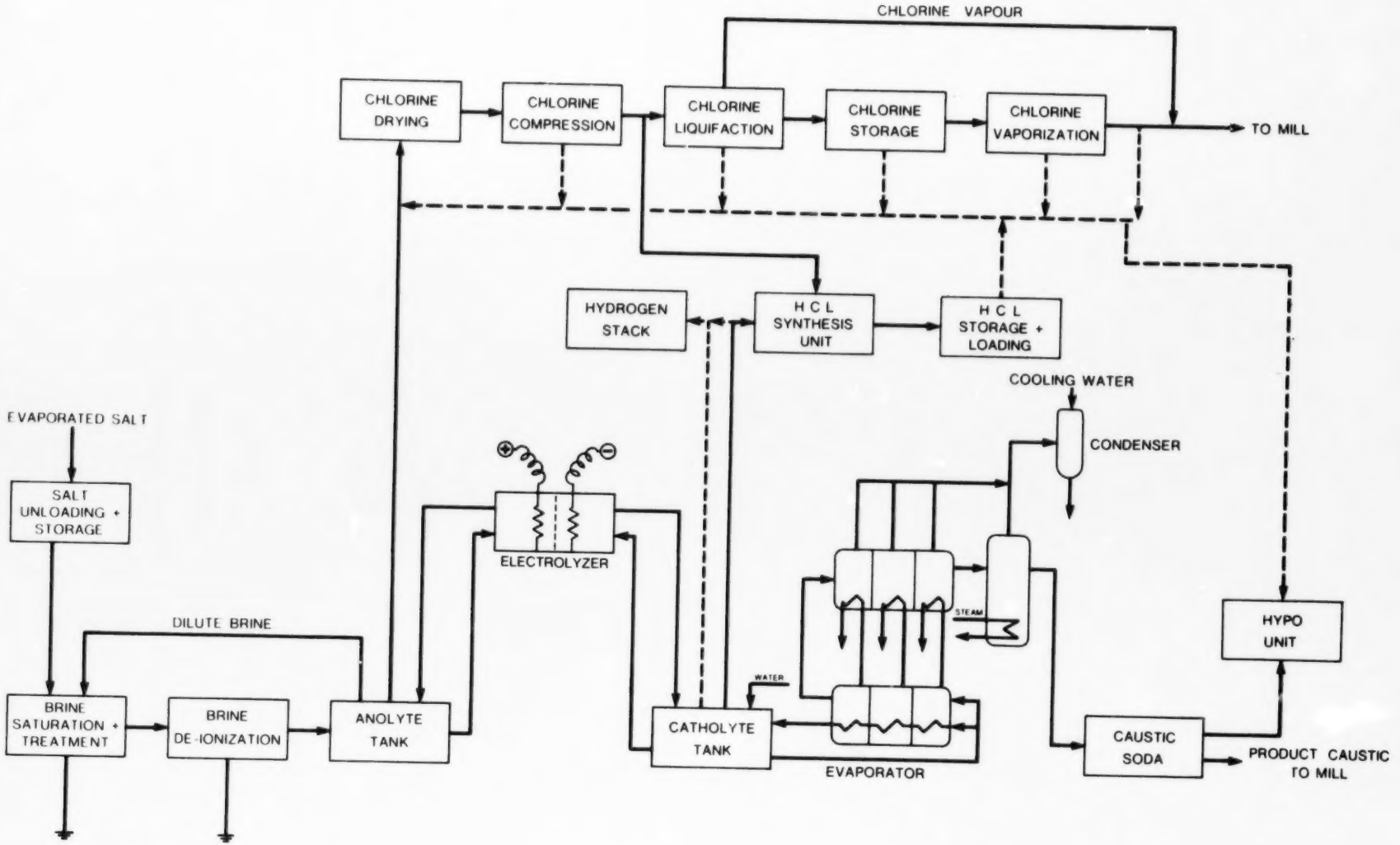


FIGURE 6 CHLORINE-CAUSTIC SODA FLOW DIAGRAM MEMBRANE CELL

Brine Deionizer Regeneration

At two of the plants multivalent cations must be removed from the brine, before its entering the electrolyzer, by using ion exchange resins. These resin beds have to be regenerated. The amount of regenerant averages 0.4 m^3 per tonne of chlorine produced. This regenerant which contains NaOH, HCl, and NaCl is discharged with the effluent at one plant and goes to a salt cavity at another plant.

Water Demineralizer Regeneration

Very pure water must be added to the catholyte circuit in membrane plants. The regeneration of the demineralizer creates a wastewater flow of about 0.04 m^3 per tonne of chlorine produced. This flow goes to the effluent discharge or to a salt cavity.

Cell Room Wastes

The major components of cell room wastes includes leaks, spills, and general housekeeping wastewaters. The amount of wastewater varies from plant to plant, and depends on operating practices.

Chlorine Cooling Condensate

Non-contact cooling of chlorine gas, which is saturated with water vapour, is practiced at all plants. The resultant condensate, which contains chlorine, is recycled to the process after chlorine recovery. No flow values are available.

Spent Sulphuric Acid

Concentrated sulphuric acid is used in the chlorine drying towers to remove residual moisture from the chlorine after first-stage cooling. In most cases, the 98 percent acid is used until its concentration reaches 70 percent. The spent acid can be regenerated for reuse (in pulp mills, or for pH control of the effluent), sold, or discharged.

Tail Gas Scrubber Liquid

A waste-gas hypochlorite absorption unit that uses either sodium hydroxide or calcium hydroxide is normally used to absorb (a) residual chlorine gas from the liquefaction process, (b) other blow-off gases, and (c) chlorine gas on plant startup or during emergencies.

This hypochlorite can be used in other plants, sold, decomposed or discharged. (No volume figures are available).

Hydrogen Condensate

Cooling of hydrogen gas for use or sale produces a condensate, which is normally recycled to the process or directed to the sewer.

Barometric Condenser Wastewater

The barometric condenser, used with the caustic evaporator, collapses the hot vapours from the evaporator, thus creating a high vacuum in the system. This requires large amounts of water. At one plant the barometric condenser water is recycled to the cooling tower. At another plant only a small percentage of the caustic is evaporated, using once-through condenser cooling water. At the third plant all the 20 percent sodium hydroxide produced is used in the adjoining pulp mill; i.e., none of the caustic is evaporated.

Boiler Blowdown

Only one plant has boiler blowdown. The steam is supplied from adjoining pulp mills at the other two plants. The blowdown at the one plant goes directly to the sewer. (No analysis was available, but this wastewater could be high in phosphates and sulphites).

Cooling Tower Blowdown

Only one plant uses cooling towers. The blowdown from this tower passes through the indirect sulphuric acid coolers, before being discharged to the sewer. (No volume discharge figures were available.)

Sanitary Effluent

Sanitary effluent from the membrane cell plants either goes to septic tanks or the sewers.

Storm Runoff

The quantity and quality of the storm water runoff from these plants is site-specific.

At one plant the storm water enters a pond, where solids settle out, but no pH adjustment is made. At the other two plants most of the runoff joins the final discharge stream.

Summary of Wastewaters Flows

Wastewater flows, which includes process wastewater, cooling tower blowdown, boiler blowdown (if present), wastes from water treatment facilities, barometric condenser wastewater, and runoff from the plant site averages about 2500 liters per tonne of chlorine produced.

4.3 Conventional Pollutants - Methodology

The collection of detailed analytical data on conventional pollutants in process wastewater streams from membrane cell plants is very limited.

One plant, which is relatively new, has not been monitored, thus only estimated concentrations are included.

One of the other two plants has only been monitored for mercury loadings over the past two or three years. Other contaminant levels have not been monitored as the final effluent goes to the pulp and paper final-effluent treatment system.

The third plant is monitored each day by the company and periodically by government agencies. The data appears, in Section 4.4 of this report.

4.4 Description of Specific Plants

The following discussions covers plant practices in water pollution control and treatment of wastewater from membrane cell chlor-alkali plants operating in Canada.

Plant No. 1

Plant No. 1 has produced caustic soda and chlorine for 17 years by the mercury cell process. In 1978 this plant converted to the ion-exchange membrane process.

At this plant saturated brine from the brine wells is pumped into a reaction tank where soda ash and sodium hydroxide are added to precipitate calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). The brine is then pumped to a clarifier, where the solids settle out, and are periodically drawn from the bottom of the tank, mixed with spent brine, and pumped back down to the salt cavity. Some of the clarifier overflow is filtered and sent to a holding tank. The remainder is recycled to the salt cavity. Backwash from the brine filter also goes to the salt cavity.

It is most important in the membrane process to have pure brine. Thus, before entering the cell, the concentration of the multivalent cations such as calcium, magnesium, iron, and aluminum has to be maintained as low as possible in the anolyte.

Therefore, the conventionally treated brine is further treated by ion-exchange resin to remove these multivalent cations.

The depleted brine from the cells passes through a vacuum dechlorinator and air blowing tank, before being recycled to the anolyte tank. The chlorine gas from the dechlorinator joins the main chlorine stream. The chlorine gas from the air blowing tank goes to the tail gas scrubber.

A bleed is taken from the depleted brine circuit and sent to the down-well holding tank, where sodium sulphite is added to destroy any residual chlorine.

Periodically the brine deionizer has to be regenerated. This wastewater, which contains sodium chloride, hydrochloric acid, and sodium hydroxide, is sent to the brine wells.

Part of the high-purity caustic soda solution from the catholyte tank, which is at a concentration of about 21 percent, is concentrated to around 41 percent by passing the caustic solution through the heat recovery multi-effect evaporators. The caustic is further concentrated to 50 percent by passing it through a finishing evaporator. The condensate recovered from the evaporators is recycled to the catholyte tank.

Barometric condenser water, used to create a reduced pressure for the operation of the multiple effect evaporators, is recycled to the cooling water loop.

Hot, wet chlorine gas from the anolyte tank passes through an indirect titanium cooler, sulphuric acid drying towers and mist eliminator. The gas is then compressed, liquefied and stored to be either used or sold. The condensate from the chlorine cooler goes to the anolyte tank. The wash from the mist eliminator and the waste sulphuric acid is stored for use in the pulp mill.

Any sniff gases from the compression, liquefaction stages, along with chlorine from the air blowing unit are scrubbed with caustic to produce sodium hypochlorite, which is sent to the pulp mill or sold.

The hot, wet hydrogen gas coming from the catholyte tank is passed through coolers. The condensate joins other cell room wastewaters. The hydrogen is either used to produce hydrochloric acid or sent to an adjoining chemical plant.

All cellroom wastewaters; i.e., leaks, spills, general cleanup wastewaters etc., are collected and sent to the salt cavity.

Cooling tower blowdown is passed through the sulphuric acid indirect coolers and then goes to the river. This stream is joined with other sources of wastewater: boiler blowdown, boiler water softener backwash, process water softener backwash, and water used for utility and maintenance.

Storm runoff is collected in a pond where solids settle out. If the mercury concentration is too high, the effluent can be sulphide treated. When necessary a bleed is sent to the river.

Sanitary effluent goes to a septic tank. Overflow from the tank joins the main effluent discharge.

Monitoring and sampling equipment take a daily composite sample of all wastewaters discharged. The data are presented in Table 27.

Plant No. 2

At Plant No. 2 dechlorinated brine at a pH of around 9.0 is pumped to one of two saturators in parallel. Rock salt of about 98.7 percent purity is dissolved in the upflowing brine. The saturated brine is filtered to remove any solids and debris, and then flows to a reaction tank, where barium carbonate and sodium carbonate are added to remove iron, sulphate, calcium, magnesium, and other minor impurities. The overflow from this tank goes to a second reaction tank where the removal of impurities continues. Brine from the second reaction tank is passed through two filters, a heat exchanger, and is then stored in a brine retention tank where further settling of solids can take place. Brine from this tank is once again filtered, and then pumped to a head tank from where it flows to the cells. Spent brine from the cells flows to the brine receiver tank, where HCl is added to start the removal of chlorine gas. The spent brine is then pumped to a vacuum degasifier for further removal of chlorine. (The chlorine gas, removed in the vacuum degasifier and retention tank, joins the main chlorine stream from the cells). The spent brine then flows to an air degasifier tank, where air is blown up through the spent brine to complete the removal of chlorine. This weak chlorine gas is used to produce sodium hypochlorite. The dechlorinated brine goes back to the saturators.

Periodically solids from the saturators, reaction tanks, holding tank, and the brine filter backwash are sent to a sludge holding tank. These solids are then pumped over to a large clarifier used for the treatment of effluents. Solids from the clarifier underflow are vacuum-filtered and sent to a landfill. The filtrate is recycled to the clarifier to be sent later to a large aerated stabilization pond.

Chlorine is formed at the dimensionally stable anodes and removed via the anolyte tank. The hot, wet chlorine is cooled in an indirect cooler to remove water which is recycled to the brine circuit, dried in sulphuric acid towers, and then compressed and liquefied. The presence of small amounts of air and inert gases results in a residual gas

TABLE 27 POLLUTANT CONCENTRATIONS AND LOADINGS AT PLANT NO. 1, MEMBRANE CELL CHLOR-ALKALI PLANT

	STORM WATER OVERFLOW				FINAL EFFLUENT		
Parameter	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/yr)	No. of Values	Avg. Conc'n (mg/L)	Range (mg/L)	Loading (kg/kkg)
Flow	896	m^3/yr			455	m^3/d	
pH	5.9	1.3-8.7		210	9.4	2.2-11.7	
Conductivity (micromhos/cm)	57600	11000-100000		210	2630	800-24000	
Chloride	13550	3000-24900	12140	210	475	75-3780	3.00
Sodium	13500	3200-23400	12100	210	488	60-3120	3.08
Alkalinity	2000			210	200		
Mercury	0.110	0.012-0.307	0.099	210	0.008	0.001-0.029	0.00005
Chromium	0.317		0.284	210	0.120	0.010-0.580	0.00076
Residual Chlorine	8	0-18	7.17	210	2.6	0-46	0.016

containing some chlorine after liquefaction. This tail gas is used to produce sodium hypochlorite for the pulp mill, or hydrochloric acid for the chlor-alkali plant.

In the drying towers 98 percent H_2SO_4 is used in a counter-current fashion to remove water vapour from the chlorine. The spent acid from the first tower at about 70 percent H_2SO_4 is currently sent to the sewer. The use of this acid in the pulp mill is being planned.

Pure caustic soda, coming from the cells at a concentration of about 10 percent, is sent to a storage tank. The caustic soda required by the pulp mill is pumped over to storage tanks in the mill. The remaining caustic soda is concentrated to 50 percent in multi-effect evaporators, and stored for later sale. The condensate from the evaporators is sent to the boiler house. The barometric condenser water, used to create a vacuum for the operation of the multi-effect evaporators, is discharged to the sewer.

Hydrogen, generated at the cathode, is removed from the process at the catholyte tank and cooled in an indirect cooler. Some of the hydrogen gas is then compressed for use in the production of hydrochloric acid. The remainder of the hydrogen gas is vented to the atmosphere. Condensate produced when the hot, wet hydrogen is cooled, is recycled to the plant or discharged to the sewer, depending on the water balance.

Cooling water used in the refrigeration unit, hypochlorite heat exchanger, etc. is recycled to the water filtration plant.

Sanitary effluent goes to the municipal system or is discharged to the pulp and paper clarifier.

Backwash from the ion-exchange soft-water process is discharged to the sewer. This wastewater joins the wastewaters from storm runoffs, cell room and brine treatment area, and utility and maintenance area. These combined wastewaters are monitored for flow and some other parameters regularly, before they enter the clarifier.

Plant No. 3

Plant No. 3 uses metal anodes and a perfluorocarboxylic acid membrane. The cell is fabricated from titanium and steel (like the Asahi cell used in Plant No. 1). Thus the chances of producing chlorinated organics are remote. Any metals present in the salt or from corrosive attacks on equipment are removed by the ion-exchange resin and discharged with the brine deionizer regenerant that joins the effluent stream before entering a retention pond.

At this plant, evaporated salt of over 99 percent purity is used for brine make-up. However, since the membrane process requires brine free of multivalent cations, such as calcium, aluminum, magnesium, and iron (to prevent plugging of the membrane), the dissolved salt is first treated with soda ash and caustic soda to precipitate calcium carbonate and magnesium hydroxide. After filtration, additional treatment is attained by the use of ion-exchange resin to remove any residual multivalent cations.

Brine sludges and filter backwash, which are discharged to the sewer, contain an estimated 500 kg/d NaCl, 5 kg/d $Mg(OH)_2$, 65 kg/d $CaCO_3$, and 30 kg/d alpha-cellulose filtering aid.

The brine deionizer regenerants are also discharged to the sewer. This wastewater contains an estimated 3000 kg/d NaCl, 350 kg/d HCl and 360 kg/d NaOH.

The caustic soda produced by this process is claimed to be quite pure; however, during shutdowns the cathode surfaces are slightly corroded, thus some iron appears in the NaOH product. The iron and other impurities are removed by filtration. The backwash from this filter is discharged to the sewer.

The chlorine removed from the dechlorinator and the tail gas are scrubbed with NaOH to produce sodium hypochlorite. This hypochlorite is normally sent to the chlorate plant. At times the hypochlorite has to be discharged to the sewer.

The water demineralizer regenerant is also discharged to the sewer. The estimated wastes discharged with these wastewaters are 35 kg/d HCl and 35 kg/d NaOH.

Chlorine cooler condensate is recycled to the brine circuit.

Hydrogen cooler condensates are discharged to the sewer.

All cooling water used in the plant is recycled to the pulp mill.

Runoff from around the developed plant property enters the sewers.

4.5 Priority Pollutants and Biological Testing

As previously indicated, none of the membrane cell plants were monitored for priority metals or organic pollutants, nor was biological testing conducted.

From an environmental viewpoint, however, the cell represents an improvement over the mercury cell, graphite/asbestos, or dimensionally stable anodes (DSA)/asbestos cell. Mercury (from the mercury cell) and asbestos, graphite particles, and the Na_2SO_4 and NaCl stream produced during the evaporation process (from graphite/asbestos or DSA/asbestos cells) are all eliminated.

In addition, since the membrane cells use DSA, chlorinated hydrocarbons are also eliminated or greatly reduced.

4.6 Pollution Abatement Options and Treatment Technology

4.6.1 Conventional Pollutants. As already mentioned for mercury cell and diaphragm cell plants, total waste reduction depends on in-process control, isolation, treatment, and recycle or reuse, or both.

Since these three plants are associated with pulp and paper mills many abatement practices are carried out in conjunction with the pulp mill treatment systems. The abatement practices are listed below.

Brine Treatment Solids

The major raw material for the membrane cell process is a nearly saturated solution of sodium chloride. The purity of the raw salt influences the amount of inert or unusable components that must be discharged as waste. One plant has taken advantage of this fact by using evaporated salt as makeup. Another plant uses solution-mining and returns all brine purification solids and filter backwash to the salt cavity. The two plants using evaporated or rock salt filter the brine solids from the brine and send these inert solids to the pulp and paper treatment system, where the solids settle out in a pond or are filtered and sent to a landfill site. The spent brine from the chlor-alkali cells is recycled to the saturator or to the salt cavity for replenishment. Salt losses are kept to a minimum by filtering the solids from the brine.

Cell Room Wastewaters

Cell room wastes, including spills, leaks, area washdown, cell wash-waters, etc., contain no asbestos or lead, because membrane cells use ion-exchange diaphragms and dimensionally stable anodes.

Spent Sulphuric Acid

Spent sulphuric acid from two of the plants is used in the pulp mills. The other plant is planning to use the spent acid in the mill.

Tail Gas Scrubber Liquid

The sodium hypochlorite produced at the three plants is used either in the pulp mills or in the chlorate plants.

Caustic Soda

The caustic soda produced with membrane cells is very pure, requires no filtration, and can be used, as produced, for the adjoining pulp mills. The caustic,

concentrated to 50 percent at one of the membrane cell plants, requires no sulphate purge; there are no wastewaters from filter backwash or from salt separation as is common in diaphragm cell plants.

DSA Anodes

In common with other cells, the use of dimensionally stable anodes produces no chlorinated hydrocarbons in the chlorine circuit.

Brine Deionizer Regeneration

When the resin beds that are used to remove cations from the conventionally treated brine are regenerated, the effluent - containing sodium hydroxide, hydrochloric acid, sodium chloride, and weak concentrations of cations, such as iron, aluminum, calcium etc. - is discharged to the main effluent stream at one plant and to a salt cavity at another plant.

Water Demineralizer Effluent

The regeneration of the demineralizer creates an effluent containing high concentrations of sodium, calcium, and magnesium chlorides as well as minor amounts of sodium sulphate, iron, aluminum and manganese salts. These wastewaters are discharged to a salt cavity at one plant and to the effluent at the other two plants.

Hydrogen Cooler Condensate

This effluent, which is relatively free of all contaminants, is recycled to the process or discharged to the sewer.

Chlorine Cooler Condensate

The condensates are recycled at all plants.

Barometric Condenser Wastewater

Barometric condensers are used at only two plants. At one plant the condenser water is recycled to a cooling tower. At the other plant, only a small amount of caustic is evaporated. The wastewater, containing a small amount of caustic soda carry-over, is discharged to the sewer.

4.6.2 Priority Pollutants. No monitoring for toxic pollutants was undertaken at any of the membrane cell plants. Since dimensionally stable anodes and titanium-steel

electrolyzers are used, metallic pollutants in wastewaters should be at very low concentrations.

In common with other cells using DSA, no chlorinated organics are produced in the chlorine purification process.

4.6.3 Selection of Appropriate Technology. No changes in treatment technology are recommended for the three membrane cell plants. Since the three plants are associated with pulp and paper mills most pollutant streams are used in the pulp mills (i.e. waste acid and tail gas scrubber effluent) or discharged to the effluent treatment systems of the pulp mill. The one plant that is removed from the pulp mill sends most process effluents to the salt cavity from where they are recycled. All surface waters are strictly monitored and treated for mercury removal, because this plant produced caustic chlorine by the mercury cell process before 1979.

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GLOSSARY

Aberration (chromosome): An irregularity of chromosomes that causes a duplication, deletion, exchange, or other alteration of the genetic material.

Acute Toxic Effect: A reaction to exposure of short-term duration which results in immediate effects that last for a short duration with little tissue reaction.

Ames Assay: A well-known short-term test that measures a chemical's ability to cause mutations in a specially engineered strain of the bacteria Salmonella typhimurium.

Antagonism: An interaction of two or more substances such that the usual action of any one of them on living cells or tissue is altered.

Background Concentration Level: The normally occurring concentration level of a substance in a given environment and medium.

Bacteria: One-celled organism with no chlorophyll that multiply by cell division.

Base-Pair Substitution: Gene mutation in which one base-pair in DNA (such as adenine-thymine) is replaced by another (such as guanine-cytosine).

DNA CCA GGG CCC AAA GTG AAA -- Base-pair → CCA GAG CCC AAA GTG AAA --
GGT CCC GGG TTT CAC TTT --- Substitution GGT CTC GGG TTT CAC TTT --

CTC - specifies wrong amino acid

"The altered base sequence that results from a base-pair substitution often leads to a change in amino acid sequence in the protein that is encoded by the gene. The altered protein may function differently from the original protein, thereby causing a difference in the characteristics of the organism.12

Best Practicable Technology (BPT): The set of end-of-process industrial controls judged to perform best in the context of maximum results weighed against feasible cost.

Bioassay: A test to determine the effect of a chemical on a living organism.

Biodegradable: Having the ability to breakdown or decompose rapidly under normal environmental conditions and processes.

Carcinogen(ic):	An agent capable of producing cancer in a tissue upon exposure.
Chromosome:	A form of DNA organization found in higher cells and organisms.
Chronic Exposure:	Prolonged or repeated exposure over a long-term duration.
Chronic Toxic Effect:	A reaction to exposure which results in prolonged effects characterized by pathological tissue changes for which little or ineffective repair is possible, or which continue to worsen.
Co-carcinogen:	An agent, not itself a carcinogen, which enhances the action of a given carcinogen when present in an administered mixture with that carcinogen.
Cumulative (or bio-accumulative):	A toxicant tending to allow accumulation, especially within a functioning life system.
DNA (deoxyribonucleic acid):	A large molecule that contains the genetic information responsible for cell growth and function.
Enzyme:	A protein that acts as a catalyst to facilitate a specific chemical reaction to take place in a cell.
Epidemiology:	The science of correlating exposure to a substance with the appearance of a specific disease or other effect in a human population group.
Estimated Permissible Concentration (EPC):	The estimated level of a substance for continuous exposure that will not result in toxic effects to humans or to the ecology.
False negative:	A test result which indicates that a chemical is harmless when it is actually hazardous.
False positive:	A test result which indicates that a chemical is hazardous when it is actually harmless.
Fractionation:	The process of chemically separating a complex mixture into a series of simpler mixtures (fractions).
Frameshift:	One or a few base-pairs are added to the structure of DNA or deleted from it.

DNA CCA GGG CCC AAA GTG AAA -- Frameshift CCA GGC CCA AAG TGA AA----
GGT CCC GGG TTT CAC TTT ---→ GGT CCG GGT TTC ACT TT----------

Base-pair deletion
CCG GGT TTC - Specifies wrong amino acids
ACT - Specifies no amino acids.

"A frameshift mutation alters all of the genetic information after the point in the DNA at which a base pair is added or deleted. Consequently frameshift mutations lead to grossly altered and non-functional gene products". (12)

Genes: Units of chromosomes that determine and mediate heredity.

Genotoxins: Chemical substances that affect genes. Used to refer to those agents reported to be oncogenic, teratogenic, or mutagenic.

Hazard Assessment: The evaluation process for determining if a substance is hazardous to humans.

In Vitro: Pertains to a procedure that takes place in an artificial medium (lab equipment) without the use of live animals. Literally means "in glassware".

In Vivo: Pertains to a biological reaction or test which occurs within the body of a live animal.

LC_{50}: The calculated concentration of a substance in either air or water (as separate figures) which will cause the death of 50 percent of an experimental animal population under controlled conditions and time exposure, most often 96 hours for aquatic species. (The 50 may or may not be subscripted.)

LD_{Lo}: The lowest recorded dose of a substance reported to cause death in humans or animals exposed for any duration by any route other than inhalation. The Lo may or may not be subscripted.)

LD_{50}: The lethal dose to 50 percent of a population; the calculated dose of a chemical substance which is expected to cause the death of 50 percent of an entire population of an experimental animal species as determined from exposure to the substance by any route other than inhalation. (The 50 may or may not be subscripted.)

Metabolic Activation: The process whereby an inactive material is changed into an active one (in the context of short-term testing, this involves the conversion of a procarcinogen to a carcinogen or a promutagen to a mutagen).

Metabolism:	The physical and chemical processes in an organism which transform chemicals into simpler or more complex forms.
Mutagenic:	Resulting in a permanent change in hereditary material involving a physical change in chromosome relations, a fundamental change in the arrangement of genes, or an alteration in the makeup of DNA.
S-9 (liver homogenates):	For general mutagenesis screening liver homogenates from rats induced with a polychlorinated biphenyl (PCB) mixture (Aroclor 1254) is used. Other tissues have been used, however, rat liver is the most convenient source of activating enzymes. It is essential for efficient detection of a wide variety of carcinogens requiring metabolic activation. It has been found that liver from Aroclor-induced rats is the most efficient for detecting different classes of carcinogens.
Synergism:	The ability of a substance to achieve or cause an appreciably different or greater effect than its own usual effect when present in conjunction with another substance.
Teratogenic:	Inducing structural and/or functional deviation in an embryo during its development, resulting in congenital birth defects.
Toxicity:	The ability of a chemical molecule or compound to produce injury once it reaches a susceptible site in or on the body.
Toxicology:	The study of the actions, detections, and treatment of poison and poisonings.

APPENDIX A

TABLE A1 LIST OF TOXIC POLLUTANTS*

Name of Compound and Elements

1. Acenaphthene
2. Acrolein
3. Acrylonitrile
4. Benzene
5. Benzidine
6. Carbon tetrachloride (tetrachloromethane)
7. Chlorobenzene
8. 1,2,4-Trichlorobenzene
9. Hexachlorobenzene
10. 1.2-Dichloroethane
11. 1,1,1-Trichloroethane
12. Hexachloroethane
13. 1,1-Dichloroethane
14. 1,1,2-Trichloroethane
15. 1,1,2,2-Tetrachloroethane
16. Chloroethane
17. Bis(chloromethyl) ether
18. Bis(2-chloroethyl) ether
19. 2-Chloroethyl vinyl ether (mixed)
20. 2-Chloronaphthalene
21. 2,4,6-Trichlorophenol
22. Parachlorometa cresol
23. Chloroform (trichloromethane)
24. 2-Chlorophenol
25. 1,2-Dichlorobenzene
26. 1,3-Dichlorobenzene
27. 1,4-Dichlorobenzene
28. 3,3'-Dichlorobenzidine

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*Taken from the report "Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemical Manufacturing," Point Source Category, EPA 440/1-79/007.

29. 1,1-Dichloroethylene
30. 1,2-Trans-dichloroethylene
31. 2,4-Dichlorophenol
32. 1,2-Dichloropropane
33. 1,2-Dichloropropylene (1,3-dichloropropene)
34. 2,4-Dimethylphenol
35. 2,4-Dinitrotoluene
36. 2,6-Dinitrotoluene
37. 1,2-Diphenylhydrazine
38. Ethylbenzene
39. Fluoranthene
40. 4-Chlorophenyl phenyl ether
41. 4-Bromophenyl phenyl ether
42. Bis(2-chloroisopropyl) ether
43. Bis(2-chloroethoxy) methane
44. Methylene chloride (dichloromethane)
45. Methyl chloride (chloromethane)
46. Methyl bromide (bromomethane)
47. Bromoform (tribromomethane)
48. Dichlorobromomethane
49. Trichlorofluoromethane
50. Dichlorodifluoromethane
51. Chlorodibromomethane
52. Hexachlorobutadiene
53. Hexachlorocyclopentadiene
54. Isophorone
55. Naphthalene
56. Nitrobenzene
57. 2-Nitrophenol
58. 4-Nitrophenol
59. 2,4-Dinitrophenol
60. 4,6-Dinitro-o-cresol
61. N-nitrosodimethylamine
62. N-nitrosodiphenylamine
63. N-nitrosodi-n-propylamine

64. Pentachlorophenol
65. Phenol
66. Bis(2-ethylhexyl) phthalate
67. Butyl benzyl phthalate
68. Di-n-butyl phthalate
69. Di-n-octyl phthalate
70. Diethyl phthalate
71. Dimethyl phthalate
72. Benzo(a)anthracene (1,2-benzanthracene)
73. Benzo (a) pyrene (3,4-benzopyrene)
74. 3,4-Benzofluoranthene
75. Benzo(k)fluoranthane (11,12-benzofluoranthene)
76. Chrysene
77. Acenaphthylene
78. Anthracene
79. Benzo(ghi)perylene (1,12-benzoperylene)
80. Fluorene
81. Phenanthrene
82. Dibenzo (a,h)anthracene (1,2,5,6-dibenzanthracene)
83. Indeno (1,2,3-cd)pyrene (2,3-o-phenylenepyrene)
84. Pyrene
85. Tetrachloroethylene
86. Toluene
87. Trichloroethylene
88. Vinyl chloride (chlorethylene)
89. Aldrin
90. Dieldrin
91. Chlordane (technical mixture & metabolites)
92. 4,4'-DDT
93. 4,4'-DDE (p,p'-DDX)
94. 4,4'DDD (p,p'-TDE)
95. A-endosulfan-Alpha
96. B-endosulfan-Beta
97. Endosulfan sulfate
98. Endrin

99. Endrin aldehyde
100. Heptachlor
101. Heptachlor epoxide
102. A-BHC-Alpha
103. B-BHC-Beta
104. R-BHC (lindane)-Gamma
105. G-BHC-Delta
106. PCB-1242 (Arochlor 1242)
107. PCB-1254 (Arochlor 1254)
108. PCB-1221 (Arochlor 1221)
109. PCB-1232 (Arochlor 1232)
110. PCB-1248 (Arochlor 1248)
111. PCB-1260 (Arochlor 1260)
112. PCB-1016 (Arochlor 1016)
113. Toxaphene
114. Antimony (Total)
115. Arsenic (Total)
116. Asbestos (Fibrous)
117. Beryllium (Total)
118. Cadmium (Total)
119. Chromium (Total)
120. Copper (Total)
121. Cyanide (Total)
122. Lead (Total)
123. Mercury (Total)
124. Nickel (Total)
125. Selenium (Total)
126. Silver (Total)
127. Thallium (Total)
128. Zinc (Total)
129. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

APPENDIX B

TABLE B1 SALMONELLA MUTAGENICITY TEST ON MERCURY CELL PLANT STRAIGHT EFFLUENT NO. 1

Tester Strain Metabolic Activation Final Dilution of Straight Effluent	Equivalent Original Effluent Volume(ml)[b]	Number of Histidine-Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:2	0.5	6	9	84	78	12	14	7	10	39	38
1:4	0.25	9	9	79	78	13	12	11	8	44	37
1:8	0.12	8	8	75	75	13	13	10	12	40	34
1:16	0.06	8	12	92	85	15	13	10	13	41	35
1:32	0.03	13	9	73	66	12	15	9	11	42	39
Negative Control	PBS[c]	8	7	80	69	10	12	10	13	34	29
Positive Control											
NaAz	5 µg/plate	1380	-	1513	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1476	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	1733	-	1526	-
B(a)P	10 µg/plate	-	-	118	338	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

[c]PBS = phosphate buffered saline

TABLE B2 SALMONELLA MUTAGENICITY TEST ON MERCURY CELL PLANT STRAIGHT EFFLUENT NO. 2

Tester Strain Metabolic Activation Final Dilution of Straight Effluent	Equivalent Original Effluent Volume(ml)[b]	Number of Histidine-Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:2	0.5	25	21	138	154	11	6	4	10	38	27
1:4	0.25	18	17	145	132	6	6	4	11	38	30
1:8	0.12	16	19	137	146	6	8	6	7	40	26
1:16	0.06	18	18	137	144	9	8	4	9	31	33
1:32	0.03	18	17	140	130	7	6	3	9	42	27
Negative Control	PBS[c]	16	18	136	125	9	6	5	8	35	27
Positive Control											
NaAz	5 µg/plate	1398	-	1680	-	-	-	-	-	-	-
9-AA	100 u g/plate	-	-	-	-	1123	-	-	-	-	-
2NF	5 u g/plate	-	-	-	-	-	-	1145	-	1393	-
B(a)P	10 u g/plate	-	-	184	904	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

[c]PBS = phosphate buffered saline

TABLE B3 SALMONELLA MUTAGENICITY TEST ON MERCURY CELL PLANT STRAIGHT EFFLUENT NO. 3

Tester Strain Metabolic Activation Final Dilution of Straight Effluent	Equivalent Original Effluent Volume(ml)[b]	Number of Histidine-Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:2	0.5	5	9	115	111	13	6	6	10	25	27
1:4	0.25	9	9	102	119	9	6	6	6	27	26
1:8	0.12	7	10	114	120	12	6	6	8	27	25
1:16	0.06	11	10	110	113	10	6	6	6	32	26
1:32	0.03	8	9	104	120	8	9	6	6	24	29
Negative Control	PBS[c]	8	9	117	106	7	9	7	5	27	22
Positive Control											
NaAz	5 µg/plate	964	-	1064	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	678	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	618	-	698	-
B(a)P	10 µg/plate	-	-	135	713	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

[c]PBS = phosphate buffered saline

TABLE B4 SALMONELLA MUTAGENICITY TEST ON MERCURY CELL PLANT FINAL EFFLUENT EXTRACT NO. 1

Tester Strain Metabolic Activation Final Dilution of Extract[b]	Equivalent Original Effluent Volume(ml)[c]	Number of Histidine-Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:25	10	12	18	411	458	19	35	14	28	32	63
1:40	6.2	15	21	302	387	18	36	15	31	38	67
1:80	3.1	16	23	191	330	14	38	17	31	31	57
1:160	1.6	12	21	171	191	11	36	21	26	25	56
1:320	0.8	17	25	115	164	17	38	19	26	37	60
1:640	0.4	16	24	103	133	19	44	15	25	35	54
1:1280	0.2	14	28	106	129	11	41	20	31	25	54
Solvent Control	DMSO[b]	12	23	99	118	19	38	17	30	34	55
Positive Control											
NaAz	5 µg/plate	1038	-	1058	-	-	-	-	-	-	-
9-AA	100 ug/plate	-	-	-	-	1294	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	1097	-	852	-
B(a)P	10 µg/plate	-	-	88	363	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Final concentration of solvent in plate is 4% DMSO

[c]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

TABLE B5 SALMONELLA MUTAGENICITY TEST ON MERCURY CELL PLANT FINAL EFFLUENT EXTRACT NO. 2

Tester Strain Metabolic Activation Final Dilution of Extract[b]	Equivalent Original Effluent Volume(ml)[c]	Number of Histidine-Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:25	10	22	17	223	255	12	0	12	13	49	42
1:40	6.2	14	20	250	276	12	4	14	20	47	52
1:80	3.1	15	0	140	254	14	0	15	19	38	46
1:160	1.6	16	9	167	175	10	7	19	21	42	48
1:320	0.8	13	8	144	157	10	12	19	23	40	50
1:640	0.4	16	5	113	150	13	10	16	31	42	48
1:1280	0.2	12	9	113	136	11	19	11	26	38	54
Solvent Control	DMSO[b]	14	14	124	132	13	21	18	23	40	53
Positive Control											
NaAz	5 µg/plate	1232	-	1491	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1718	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	1301	-	854	-
B(a)P	10 µg/plate	-	-	136	985	-	-	-	-	-	-

[a] Mean value of colony counts from triplicate plates

[b] Final concentration of solvent in plate is 4% DMSO

[c] Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

TABLE B6 SALMONELLA MUTAGENICITY TEST ON MERCURY CELL PLANT FINAL EFFLUENT EXTRACT NO. 3

Tester Strain Metabolic Activation Final Dilution of Extract[b]	Equivalent Original Effluent Volume(ml)[c]	Number of Histidine Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:25	10	13	16	170	97	T	10	T	19	21	41
1:40	6.2	15	15	161	137	8	17	T	20	49	49
1:80	3.1	18	16	145	140	11	15	11	18	38	43
1:160	1.6	16	20	143	92	9	17	8	22	34	36
1:320	0.8	15	11	142	121	8	15	10	23	32	35
1:640	0.4	14	14	136	119	9	16	11	22	30	38
1:1280	0.2	16	15	126	140	7	14	8	29	23	37
Solvent Control	DMSO[b]	16	16	137	127	6	18	10	26	23	41
Positive Control											
NaAz	5 µg/plate	1347	-	1345	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1116	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	833	-	769	-
B(a)P	10 µg/plate	-	-	136	946	-	-	-	-	-	-

[a] Mean value of colony counts from triplicate plates

[b] Final concentration of solvent in plate is 4% DMSO

[c] Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

TABLE B7 SALMONELLA MUTAGENICITY TEST ON EXTRACT BLANK

Tester Strain Metabolic Activation Final Dilution of Extract[b]	Equivalent Original Effluent Volume(ml)[c]	Number of Histidine Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:25	10	15	16	125	91	13	10	15	24	46	40
1:40	6.2	14	14	127	104	13	17	14	16	44	49
1:80	3.1	15	10	111	107	14	22	15	22	31	48
1:160	1.6	16	17	124	70	11	19	11	24	29	40
1:320	0.8	18	17	130	110	12	19	9	21	29	42
1:640	0.4	17	12	109	109	16	17	9	18	24	34
1:1280	0.2	13	15	121	123	18	15	13	20	27	35
Solvent Control	DMSO[b]	16	14	127	121	13	15	14	22	33	41
Positive Control											
NaAz	5 µg/plate	1257	-	1283	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1032	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	684	-	769	-
B(a)P	10 µg/plate	-	-	123	828	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Final concentration of solvent in plate is 4% DMSO

[c]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

TABLE B8 CHROMOSOME ABERRATIONS IN CHINESE HAMSTER CELLS FOLLOWING EXPOSURE TO EXTRACTS OF MERCURY CELL CHLOR-ALKALI FINAL EFFLUENTS[a]

Extract No.			% Metaphase Plates with Chromosome Aberrations[b] No. 1		No. 2		No. 3	
Metabolic Activation			-S-9	+S-9	-S-9	+S-9	-S-9	+S-9
Final Dilution of Extract	DMSO Conc. in Diluted Extract (%)	Equivalent Origional Effluent Volume(ml)						
1:10	10	25	3.0	10.0	2.0	7.0	MI[c]	2.0
1:20	5	12.5	2.0	2.0	2.0	0.0	29.1[c]	0.0
1:40	2.5	6.2	1.0	0.0	0.0	d	2.0	-
1:80	1.2	3.1	0.0	-	-	-	0.0	-
1:160	1.2	1.6	-	-	-	-	d	-
1:320	1.2	0.8	-	-	-	-	-	-
1:640	1.2	0.4	-	-	-	-	-	-
1:1280	1.2	0.2	-	-	-	-	-	-
Solvent Control (DMSO)								
1:10	Dilution		0.0	0.0	1.0	2.0	0	0
1:20	Dilution		0.0	0.0	0.0	0.0	0	0
1:40	Dilution		0.0	0.0	0.0	0.0	0	0
1:80	Dilution		1.0	0.0	0.0	0.0	0	0
Control (Aflatoxin B_1)								
10^{-5} M			-	-	-	-	-	-
5×10^{-6} M			0.0	65.2	0.0	57.9	0	63.3

[a]Three hour exposure to effluent extract.

[b]A minimum of 100 metaphase plates are scored unless the number is limited as a result of mitotic inhibition.

[c]MI = mitotic inhibition; 1 metaphase in 4000 cells.

[d]- = not analyzed.

TABLE B9 DNA REPAIR TEST ON EXTRACTS OF MERCURY CELL CHLOR-ALKALI FINAL EFFLUENTS (UNSCHEDULED DNA SYNTHESIS IN CULTURED HUMAN FIBROBLASTS)

Extract No.			Average Number of Grains per Nucleus[a]							
			No. 1		No. 2		No. 3		Extract Blank	
Metabolic Activation			+S-9		+S-9		+S-9		+S-9	
Final Dilution of Extract	DMSO Conc. in Diluted Extract (%)	Equivalent Origional Effluent Volume(ml)[b]								
1:10	10	25	0	0	0	0	0	0	T	0
1:20	5	12.5	0	0	0	0	1	0	T	0
1:40	2.5	6.2	0	1	0	0	0	0	0	0
1:80	1.2	3.1	0	1	0	0	0	0	0	0
1:160	1.2	1.6	0	1	0	0	0	0	0	0
1:320	1.2	0.8	0	0	0	0	0	0	0	0
1:640	1.2	0.4	0	0	0	0	0	0	0	0
1:1280	1.2	0.2	0	0	0	0	0	0	0	0
Solvent Control (DMSO)										
1:10	10		0	2	0	0	1	0	0	0
1:20	5		0	1	0	0	0	0	0	0
1:40	2.5		0	1	0	0	0	1	0	0
1:80	1.2		0	0	0	0	0	0	0	0
Control (Aflatoxin B_1)										
10^{-4} M			1	38	0	30	1	42	0	28
10^{-5} M			1	30	0	15	0	25	0	17

[a]Minimum of 30 nuclei scored, unless otherwise stated.

[b]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture.

[c]T = toxic effects: cells changed morphology and/or detached from cover glass;
-, not analyzed; ND, no data.

TABLE B10 DNA REPAIR INHIBITION TEST ON EXTRACTS OF MERCURY CELL CHLOR-ALKALI FINAL EFFLUENTS (EFFECT ON UV-INDUCED UNSCHEDULED DNA SYNTHESIS IN CULTURED HUMAN FIBROBLASTS)

Extract No.			Average Number of Grains per Nucleus[a]							
			No. 1		No. 2		No. 3		Extract Blank	
Metabolic Activation				+S-9		+S-9		+S-9		+S-9
Final Dilution of Extract	DMSO Conc. in Diluted Extract (%)	Equivalent Origional Effluent Volume(ml)[b]								
1:10	10	25	0	45	0	0	T	47	0	0
1:20	5	12.5	5	41	5	19	21	51	19	25
1:40	2.5	6.2	26	43	6	19	46	51	47	32
1:80	1.2	3.1	30	42	10	21	50	-	50	36
1:160	1.2	1.6	28	43	11	27	50	-	51	36
1:320	1.2	0.8	30	-	15	23	51	-	50	36
1:640	1.2	0.4	44	-	20	23	51	-	51	-
1:1280	1.2	0.2	56	-	21	-	51	-	51	-
Solvent Control (DMSO)										
1:10	10		17	21	ND	26	39	38	ND	ND
1:20	5		30	28	32	29	29	45	40	34
1:40	2.5		34	32	32	ND	33	45	41	33
1:80	1.2		53	36	24	25	49	40	33	35

[a] UV dose used: 20 ergs/mm^2. Minimum of 30 nuclei scored, unless otherwise stated.

[b] Expressed as equivalent volume of original effluent per ml incubation mixture.

[c] T = toxic effects: cells changed morphology and/or detached from cover glass; -, not analyzed; ND, no data.

APPENDIX C

BLE C1 SALMONELLA MUTAGENICITY TEST ON DIAPHRAGM CELL PLANT STRAIGHT EFFLUENT NO. 1

ter Strain tabolic ivation al ution traight luent	Equivalent Original Effluent Volume(ml)[b]	Number of Histidine Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
	0.5	8	11	101	90	10	11	6	5	34	13
	0.25	8	7	99	86	5	7	7	9	25	20
	0.12	7	10	105	88	11	10	9	9	22	19
	0.06	7	10	93	80	7	5	5	8	25	14
	0.03	6	10	87	78	10	7	8	6	25	13
ative Control	PBS[c]	6	8	82	78	8	7	8	8	27	20
tive Control											
Az	5 µg/plate	815	-	963	-	-	-	-	-	-	-
A	100 µg/plate	-	-	-	-	720	-	-	-	-	-
	5 µg/plate	-	-	-	-	-	-	694	-	675	-
P	10 µg/plate	-	-	152	741	-	-	-	-	-	-

an value of colony counts from triplicate plates

pressed as equivalent volume (ml) of original effluent per ml incubation mixture

S = phosphate buffered saline

TABLE C2 SALMONELLA MUTAGENICITY TEST ON DIAPHRAGM CELL PLANT FINAL EFLUENT EXTRACT NO. 1

Tester Strain Metabolic Activation Final Dilution of Extract[b]	Equivalent Original Effluent Volume(ml)[c]	Number of Histidine Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:25	10	13	14	247	159	17	2	11	22	72	54
1:40	6.2	16	19	217	162	19	7	10	19	56	54
1:80	3.1	11	12	150	ND	18	17	9	21	43	21
1:160	1.6	10	23	135	81	14	23	7	22	50	46
1:320	0.8	12	21	129	75	20	28	11	17	46	46
1:640	0.4	9	6	89	100	15	16	8	15	34	ND
1:1280	0.2	14	13	90	106	18	22	13	20	36	24
Solvent Control	DMSO[b]	11	13	105	97	17	26	12	18	40	30
Positive Control											
NaAz	5 µg/plate	1195	-	1360	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	759	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	969	-	649	-
B(a)P	10 µg/plate	-	-	108	504	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Final concentration of solvent in plate is 4% DMSO

[c]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

TABLE C3 SALMONELLA MUTAGENICITY TEST ON EXTRACT BLANK

Tester Strain Metabolic Activation Final Dilution of Extract[b]	Equivalent Original Effluent Volume(ml)[c]	Number of Histidine Positive Revertants per Plate[a]									
		TA 1535		TA 100		TA 1537		TA 1538		TA 98	
			+S-9		+S-9		+S-9		+S-9		+S-9
1:25	10	15	16	125	91	13	10	15	24	46	40
1:40	6.2	14	14	127	104	13	17	14	16	44	49
1:80	3.1	15	10	111	107	14	22	15	22	31	48
1:160	1.6	16	17	124	70	11	19	11	24	29	40
1:320	0.8	18	17	130	110	12	19	9	21	29	42
1:640	0.4	17	12	109	109	16	17	9	18	24	34
1:1280	0.2	13	15	121	123	18	15	13	20	27	35
Solvent Control	DMSO[b]	16	14	127	121	13	15	14	22	33	41
Positive Control											
NaAz	5 µg/plate	1257	-	1283	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1032	-	-	-	-	-
2NF	5 ug/plate	-	-	-	-	-	-	684	-	769	-
B(a)P	10 ug/plate	-	-	123	828	-	-	-	-	-	-

[a]Mean value of colony counts from triplicate plates

[b]Final concentration of solvent in plate is 4% DMSO

[c]Expressed as equivalent volume (ml) of original effluent per ml incubation mixture

TABLE C4 CHROMOSOME ABERRATIONS IN CHINESE HAMSTER CELLS FOLLOWING EXPOSURE TO DIAPHRAGM CELL PLANTS FINAL EFFLUENT EXTRACTS NO. 1[a]

Extract No.			% Metaphase Plates with Chromosome Aberrations[b]			
			Blank Extract		No. 1	
Metabolic Activation				+S-9		+S-9
Final Dilution of Extract	DMSO Conc. in Diluted Extract (%)	Equivalent Original Effluent Volume(ml)				
1:10	10	25	6.0	2.0	1.0	0.0
1:20	5	12.5	2.0	1.0	1.0	0.0
1:40	2.5	6.2	1.0	0.0	0.0	-
1:80	1.2	3.1	0.0	-	-	-
1:160	1.2	1.6	-	-	-	-
1:320	1.2	0.8	-	-	-	-
1:640	1.2	0.4	-	-	-	-
1:1280	1.2	0.2	-	-	-	-
Solvent Control (DMSO)						
1:10	Dilution		0	0	0	0
1:20	Dilution		0	0	0	0
1:40	Dilution		0	0	0	0
1:80	Dilution		0	0	0	0
Control (Aflatoxin B_1)						
10^{-5} M			-	-	-	-
5×10^{-6} M			0	63.3	0	63.3

[a] Three hour exposure to effluent extract.

[b] A minimum of 100 metaphase plates are scored unless the number is limited as a result of mitotic inhibition.

[c] MI = mitotic inhibition; < 1 metaphase in 4000 cells.

[d] T = toxic effects; cells changed morphology and/or detached from cover galss.

[e] - = not analyzed.

[f] ND = no data.

TABLE C5 DNA REPAIR TEST ON EXTRACTS OF DIAPHRAGM CELL PLANT FINAL EFFLUENTS (UNSCHEDULED DNA SYNTHESIS IN CULTURED HUMAN FIBOBLASTS)

Extract No.			% Metaphase Plates with Chromosome Aberrations[b]			
			Sample No. 1		Blank Extract	
Metabolic Activation				+S-9		+S-9
Final Dilution of Extract	DMSO Conc. in Diluted Extract (%)	Equivalent Origional Effluent Volume(ml)[b]				
1:10	10	25	0	0	T	0
1:20	5	12.5	0	0	T	0
1:40	2.5	6.2	0	1	0	0
1:80	1.2	3.1	1	0	0	0
1:160	1.2	1.6	0	0	0	0
1:320	1.2	0.8	0	0	0	0
1:640	1.2	0.4	0	0	0	0
1:1280	1.2	0.2	0	1	0	0
Solvent Control (DMSO)						
1:10	10		1	0	0	0
1:20	5		0	0	0	0
1:40	2.5		0	1	0	0
1:80	1.2		0	1	0	0
Control (Aflatoxin B_1)						
10^{-4} M			1	42	0	28
10^{-5} M			0	25	0	17

[a]Minimum of 30 nuclei scored, unless otherwise stated.

[b]Expressed as equival-nt volume (ml) of original effluent per ml incubation mixture.

[c]T = toxic effects: cells changed morphology and/or detached from cover glass; -, not analyzed; ND, no data.

TABLE C6 DNA REPAIR INHIBITION TEST ON EXTRACTS OF DIAPHRAGM CELL PLANTS FINAL EFFLUENTS (EFFECT ON UV-INDUCED UNSCHEDULED DNA SYNTHESIS IN CULTURED HUMAN FIBROBLASTS)

Extract No.			Average Number of Grains per Nucleus[a]			
			Sample No. 1		Blank Extract	
Metabolic Activation			+S-9			+S-9
Final Dilution of Extract	DMSO Conc. in Diluted Extract (%)	Equivalent Origional Effluent Volume(ml)[b]				
1:10	10	25	15	38	0	0
1:20	5	12.5	41	38	19	25
1:40	2.5	6.2	42	43	47	32
1:80	1.2	3.1	45	41	50	36
1:160	1.2	1.6	ND	41	51	36
1:320	1.2	0.8	43	41	50	36
1:640	1.2	0.4	45	-	51	-
1:1280	1.2	0.2	45	-	51	-
Solvent Control (DMSO)						
1:10	10		39	38	ND	ND
1:20	5		29	45	40	34
1:40	2.5		33	45	41	33
1:80	1.2		44	38	33	35

[a] UV dose used: 20 ergs/mm^2. Minimum of 30 nuclei scored, unless otherwise stated.

[b] Expressed as equivalent volume of original effluent per ml incubation mixture.

[c] T = toxic effects: cells changed morphology and/or detached from cover glass; -, not analyzed; ND, no data.